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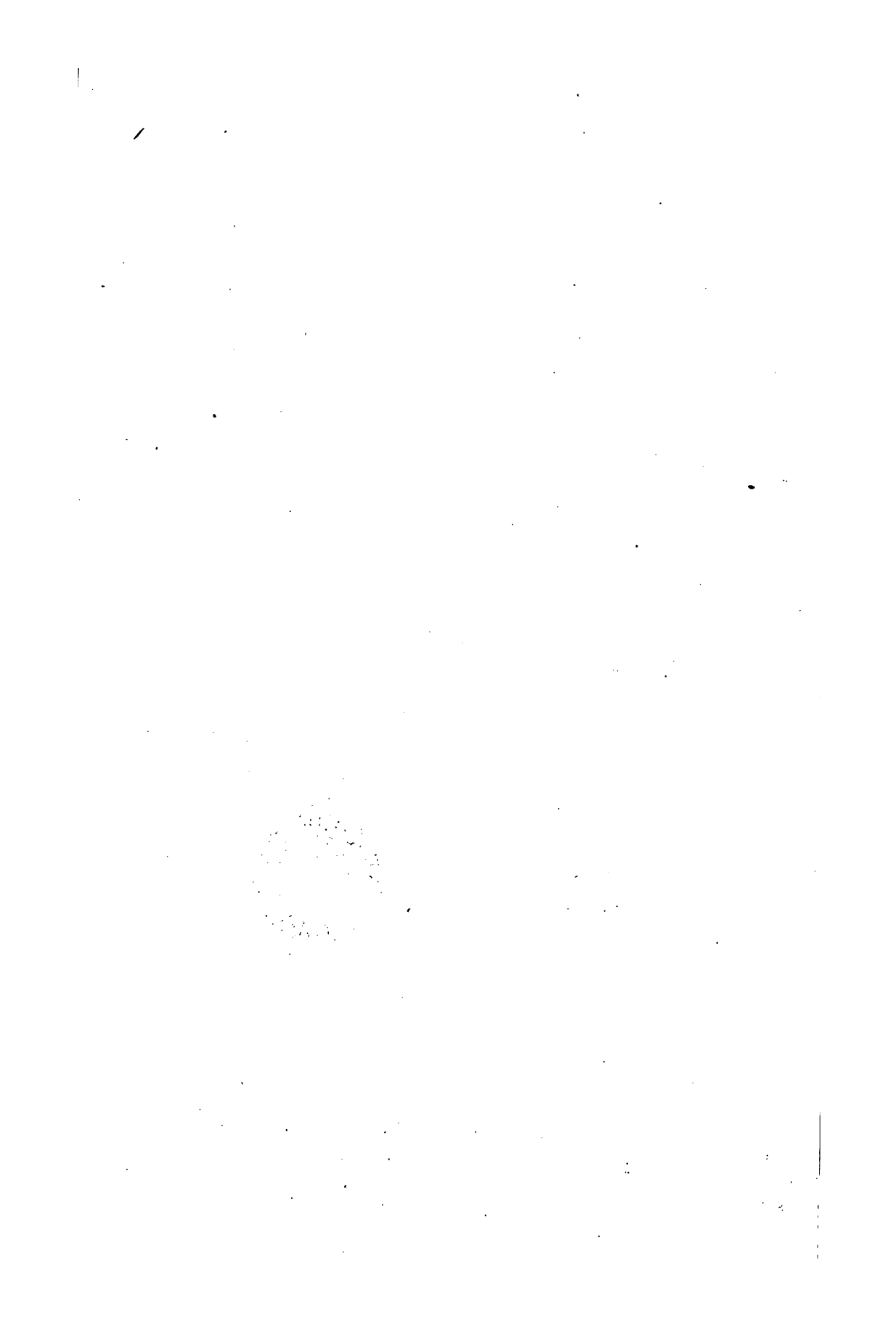
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INTRODUCTION

TO

INORGANIC CHEMISTRY

*With 82 Engravings on Wood*

BY

WM. GEO. VALENTIN, F.C.S.

PRINCIPAL DEMONSTRATOR OF PRACTICAL CHEMISTRY IN THE ROYAL SCHOOL OF MINES AND  
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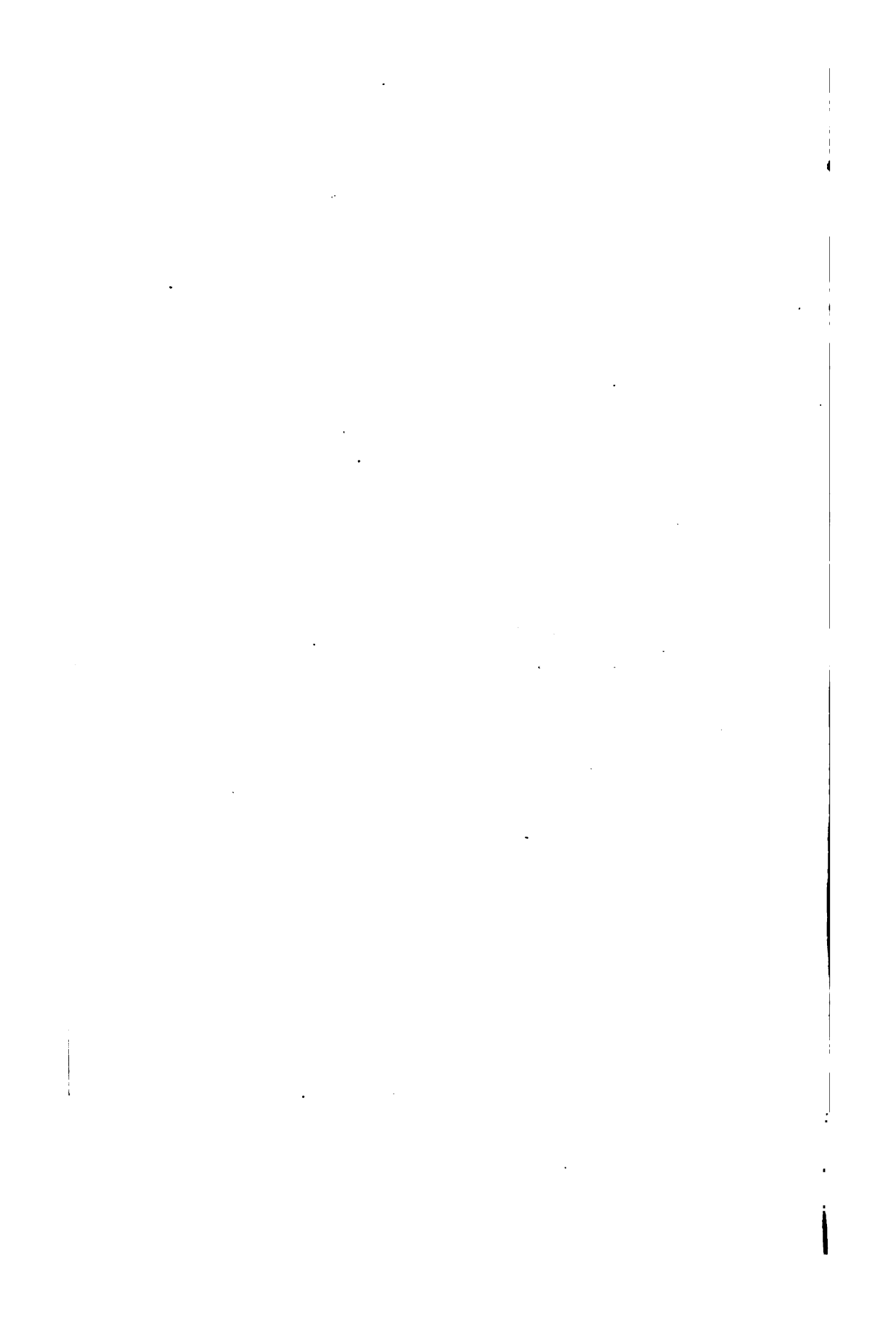
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## P R E F A C E.

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THE encouraging reception which my Laboratory Text Book met with in this country, as well as in America, and the experience which I since have had of its working with a large class of chemical students, have induced me to render the book still more generally useful by publishing it in two parts, and by somewhat enlarging the first part. I am in hope that this first volume may now take rank as a suitable text book for elementary classes preparing for the chemical examinations which are held annually under the Science and Art Department. The admirable list of experiments, sketched out by Dr. Frankland, in the Syllabus issued by the Department, will be found interwoven throughout the text. This I was able to do without deviating from the original plan of the book, which consists mainly in deducing the fundamental laws of chemistry from experimental facts, and thus to lay a sound foundation for qualitative and quantitative analyses. From my own laboratory experience, I can confidently recommend this experimental method of teaching. Large classes of students can be instructed with comparative ease, and theoretical difficulties, which are usually overcome only by a long course of chemical study, may be grappled with at the earliest stages even. I have found the theory of atomicity of chemical elements remarkably conducive to a quick and thorough understanding of chemical changes. Graphic illustrations, I need scarcely remark, may be discarded as soon as they have fulfilled their purpose, and as soon as the pupils have become familiar with the use of the constitutional symbolic formulæ employed in this work.



The Questions and Exercises, placed at the end of most of the chapters, constitute an essential feature of the book. They will be found of great use if the written answers are examined by the teacher, and any shortcomings discussed with the pupils. This entails, no doubt, much labour, but it forms, in my experience, the only safe means of controlling and rendering the laboratory teaching thoroughly efficient.

Most of the experiments can be readily performed by beginners, if the directions given in the text are attended to, others again, are perhaps more suited to the lecture-room. The selection may, however, be safely left to each teacher.

When the chemical instruction in schools or elementary science classes has, of necessity, to be conducted by lectures only, this little book will, when placed in the hands of the pupils, also form a useful companion and guide for private study.

The final chapter contains a brief summary of all the previous experimental facts, classified under four chemical changes, a summary which, I trust, will recommend itself to the practical teacher.

In conclusion, I have to thank Mr. A. J. Greenaway, Junior Assistant in the Laboratory, for his kind help in preparing a number of new wood-cuts.

CHEMICAL LABORATORIES,  
SCIENCE SCHOOLS,  
SOUTH KENSINGTON,  
Oct. 18, 1872.

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# INTRODUCTION

TO

## INORGANIC CHEMISTRY.

### CHAPTER I. HYDROGEN.

**Experiment 1.**—Fill a glass cylinder or test-tube with water, and invert it over a basin containing water, by first closing its mouth with a glass plate (Fig. 1). Wrap up a small piece of the metal sodium in a little fine wire gauze, fastened to a piece of wire. Introduce the sodium rapidly underneath the mouth of the cylinder (Fig. 2). Gas bubbles are observed to ascend through the water, and to collect in the upper part of the cylinder. The evolution of gas ceases after a few moments, and the sodium is found to have disappeared entirely. By repeating this operation, if necessary, the whole of the water in the cylinder may be replaced by a colourless gas. This gas is *hydrogen*.

A few other metals, such as potassium, barium, strontium, calcium and magnesium, decompose water likewise at the ordinary temperature with the evolution of hydrogen, but the action is, for the most part, much slower, and has, in the case of the latter metal, to be assisted by employing hot instead of cold water.

Some metals, such as aluminium, iron,

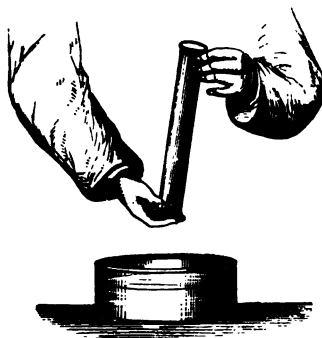


FIG. 1.

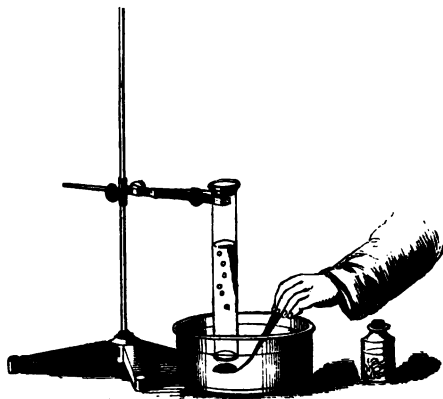


FIG. 2.—DECOMPOSITION OF WATER BY SODIUM  
B

manganese, cobalt, nickel, zinc, cadmium, tin, and antimony, which, when cold, are, for the most part, without action upon water, are yet capable of decomposing it when water, in the form of vapour or steam, is slowly passed over the metals heated to redness in a porcelain tube. They decompose it, however, more or less rapidly in the cold, if a little hydrochloric acid be added to the water. A brisk evolution of hydrogen ensues.

Other metals, again, such as copper, mercury, gold, and platinum, even when placed in acidulated water, do not evolve any hydrogen.

**Experiment 2.**—Larger quantities of hydrogen are most conveniently prepared by acting upon zinc or iron with dilute hydrochloric acid. An apparatus, represented in Fig. 3, consisting of a two-necked bottle—so-called Woulfe's bottle—is employed, fitted up by means of perforated corks with a funnel and delivery-tube. The funnel-tube reaches nearly to the bottom of the Woulfe's bottle, and serves for the introduction of the acid. The delivery-tube, which has been bent, as seen in Fig. 3, in the gas-flame of an ordinary fish-tail or bat's-wing gas-burner, is fitted into the other hole, so as just to pass through the cork. Sound and well-fitting corks should be selected for such experiments, and they ought to be well squeezed before being bored. The glass funnel and delivery-tube should readily pass through the holes, and yet fit perfectly air-tight. It is best, therefore, to bore the holes by means of a sharp cork-borer of the size of the glass tubing to be employed.

The delivery-tube dips under the water, and delivers the gas into the cylinder inverted over water in a pneumatic trough.

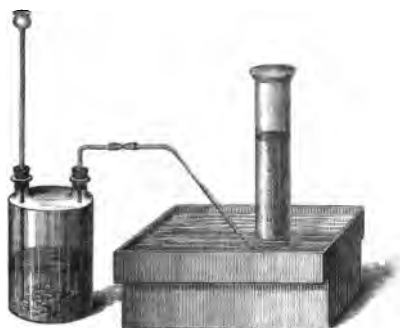


FIG. 3.—PREPARATION OF HYDROGEN FROM ZINC AND HYDROCHLORIC ACID.

Granulated zinc (or strips of sheet zinc) is introduced into the bottle, and the cork and delivery-tube adjusted properly. Moderately concentrated hydrochloric acid is then poured through the funnel-tube, when the evolution of hydrogen begins at once. The gas finding no other outlet, passes through the delivery-tube, and forces its way through the water. The air contained in the Woulfe's bottle must first be displaced before any of the gas is collected. In order to ascertain whether the air has been sufficiently displaced, some of the gas is collected over water in a test-tube

in the manner already described. When quite full, the tube is withdrawn by closing the mouth with the thumb, or with a small watch glass or glass plate. If the enclosed gas burns quietly, on applying a light to it, whilst the mouth of the tube is held downwards, with a blue lambent flame, it may be considered safe to collect the gas; but should the gas in the tube burn with a slight explosion on applying a light to it, it may be taken as an indication that the air has not been sufficiently displaced from the generating apparatus.

In the place of the zinc we might have employed iron scraps, nails, borings, or filings. Hydrogen gas, generated from impure iron, possesses a most disagreeable odour, arising from the presence of carbon and sulphur in the iron, which elements, by entering into combination with a portion of the hydrogen, form

gaseous compounds, called carburetted and sulphuretted hydrogen. Pure hydrogen is inodorous, and is but very slightly soluble in water; 100 volumes of water dissolve only 1.93 volumes of the gas.

For storing up larger quantities of hydrogen, a gasholder, represented in Fig. 4, is usually employed, consisting of a cylindrical vessel, A, made of zinc or copper, connected by means of two tubes, *a* and *b*, with the open vessel, B, and supported by one or two more tubular stays, *c* and *c'*, as shown in Fig. 4; *a* and *b* can be shut off by means of stopcocks. A glass gauge, as seen in *g g'*, indicates the height of the column of water in A. By closing the opening, *d*, fitted with a screw-plug, and turning on the taps at *a* and *b*, as well as the delivery-tap at *e*, water which is poured into the vessel B makes its way into the vessel A, till it fills it entirely, and runs over through *e*. The taps at *a*, *b*, and *c* are then closed, and the gas-holder may be charged with gas by inserting the delivery-tube through the opening at *d*, after the removal of the screw-plug. The water runs out from *d* as fast as the gas enters. When full, the screw-plug is replaced, and the apparatus is ready for use.



FIG. 4.—GASHOLDER.

By keeping the top vessel, B, always well supplied with water, the gas can be discharged at pleasure from A by turning on the tap *a*, which conveys the water down to the bottom of A, and opening the tap *e* partly or fully, as may be required. The water which flows from B to A presses upon the gas, and forces it from *e*. The top vessel, B, may also serve the purposes of a pneumatic trough, and gas may be filled directly from the gas-holder into an inverted cylinder by opening the tap *b*, and allowing the gas to escape through the water into the inverted cylinder.

*Now, what are the properties of the gas which has been collected?*

**Experiment 3.**—The hydrogen gas collected in a test-tube, or glass cylinder, as described in Experiments 1 and 2, can be readily removed from the basin (Fig. 5), or pneumatic trough, by closing the opening of the cylinder with the thumb or a glass plate.

On applying a lighted candle to the mouth of the cylinder, Fig. 6, the gas burns quietly with a lambent, non-luminous flame. It is an inflammable gas.

On introducing a wax taper, as shown in Fig. 7, into the cylinder, the gas burns at the mouth quietly with a bluish flame, giving very little light, whilst the taper, on being moved upward through the flame into the hydrogen, as shown





FIG. 5.

in Fig. 8, is immediately extinguished; on withdrawing the taper again, it ignites once more when it reaches the burning gas at the mouth of the cylinder. The taper may be thus extinguished and rekindled several times in succession.

This proves *that hydrogen cannot support combustion; also, that it burns, but only where it is in contact with the air (at the mouth of the cylinder).*

**Experiment 4.**—A strong soda-water bottle, filled to about one-third its bulk with water, is inverted over the gas delivery tube, Fig. 3, until all the water



FIG. 6.

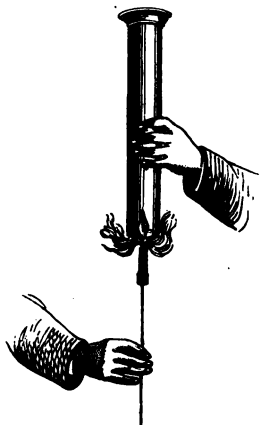


FIG. 7.

is expelled by the bubbles of gas. A mixture of air and gas in the proportion of two to one is thus obtained, which, when fired with a lighted taper, explodes with a loud report.

This proves *that a mixture of hydrogen gas and air does not combine at the ordinary temperature, but explodes with violence on coming in contact with a light.*

**Experiment 5.**—A test-tube or cylinder full of air is held, mouth downwards, and some hydrogen is allowed to pass into it from another tube, somewhat

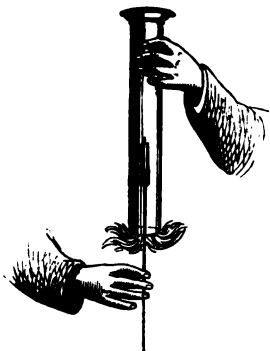


FIG. 8.

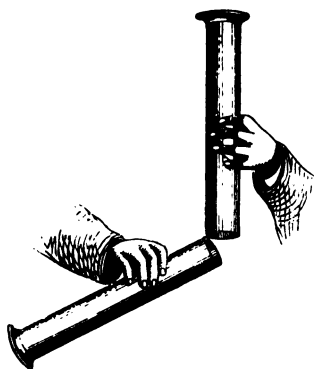


FIG. 9.

inclined, as shown in Fig. 9. On applying a light to its mouth, an explosion takes place, showing that this cylinder, which originally contained only air, contains now a mixture of hydrogen and air—a mixture which is highly explosive, as proved by Experiment 4.

This shows that the gas ascended from the lower into the upper cylinder, and that it must therefore have been *lighter than air*. Accurate determinations have established the fact, *that the gas is about 14 times lighter than air*, its specific gravity being  $\cdot 0691$ , as compared with air = 1.

Owing to its lightness it is sometimes used for filling balloons. Coal gas being, however, more easily procurable, although about 8 times heavier than hydrogen, is now usually employed for this purpose.

**Experiment 6.**—The delivery tube of the gas-generating apparatus is connected with a drying tube (containing calcic chloride, a substance which possesses a strong affinity for water), and a glass tube drawn out to a point (Fig. 10). After allowing the hydrogen to escape for some time, the jet may be lighted without any danger of an explosion.

The gas burns with a pale blue flame, which, however, is exceedingly hot. Invert a dry bell-jar over the flame. It soon becomes covered with moisture on its inner surface, and drops of condensed water collect and run down. The same may be shown by holding a wide glass tube, about

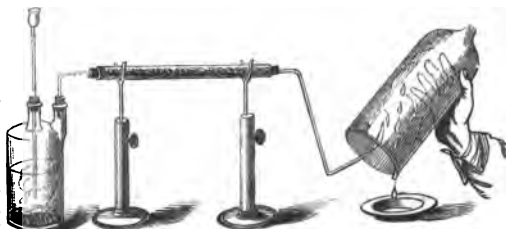


FIG. 10.

half an inch in diameter, over the jet. A musical note, high or low, according as the tube is wide or narrow, will be heard, arising from a series of small explosions, which follow one another in more or less rapid succession, as the tube is raised or lowered over the gas flame. The upper part of the tube contains the condensed water.

This proves that water is formed by the combustion of hydrogen in

air. Hence the name *hydrogen* given to the gas (from *ὕδωρ*, water, and *γεννάω*, I generate), represented shortly by the symbol H.

Bodies which consist of hydrogen, together with another element capable of burning in air, viz., carbon—usually termed hydrocarbons—such as oil of turpentine, paraffin oil, petroleum; and, again, others which contain a third element, viz., oxygen, such as common tallow, spirits of wine, wood, etc., produce all more or less water, besides some products of combustion, which will be explained hereafter. A tallow candle, *ex. gr.*, produces rather more than its own weight of water; alcohol, or spirits of wine, yields a still larger amount. This may be seen by holding a wide glass tube or a bell-jar over a burning candle, in the manner shown in Experiment 6. It is also perceived whenever water, or some other cold liquid, is heated over a spirit-lamp or gas-flame in a glass vessel (a retort or flask). Drops of water produced by the combustion of the alcohol or gas condense on the outside of the glass vessel, until the vessel has been heated sufficiently long to prevent the condensation of the water vapour or steam.

**Summary.\***—*Hydrogen is a very light gas. When pure it is colourless, tasteless, and inodorous.*

*It is inflammable, evolving much heat, but giving little light; it does not support combustion. Water is formed by its combustion in air. Although it has no poisonous properties, it cannot support life.*

## CHAPTER II.

### OXYGEN, NITROGEN, AIR.

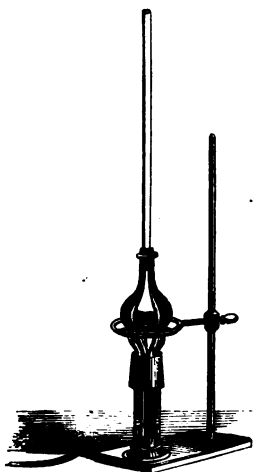


FIG. 11. OXIDATION OF MERCURY.

**Experiment 7.**—Heat a little mercury nearly to boiling in a small flask (Fig. 11) provided with a long glass tube, and shake frequently. The bright metal gets slowly coated over with a reddish-yellow film, which, on shaking, adheres to the sides of the flask, and, after heating for some hours, a portion of the metal is converted into a red powder. (The vapour of the metal mercury being poisonous, care must be taken not to allow any to escape into the room through the open condensing tube.)

On weighing the flask and metal before and after the conversion of some of the latter into the red powder, an increase in weight is observed. A ponderable substance must have been added during the heating, which can only have come from the air.

\* The summaries placed at the end of this, as well as the next following seven chapters, should be committed to memory.

**Experiment 8.**—Introduce a weighed quantity of the red powder so obtained into a tube of hard German glass (Fig. 12), and connect by means of a cork with a delivery tube, which dips under water in a pneumatic trough. On applying a strong heat to the tube by means of a Bunsen's gas burner, the at-

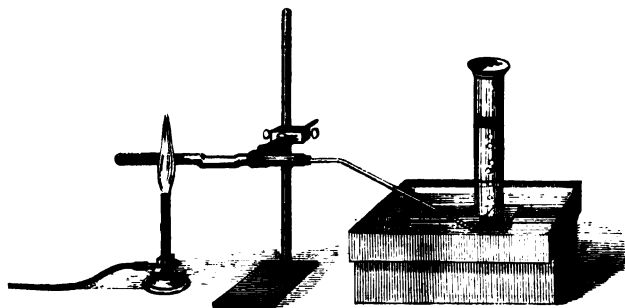


FIG. 12.—PREPARATION OF OXYGEN FROM MERCURIC OXIDE.

expands, and is forced out through the delivery tube. After a little time a metallic coating is observed to form in the bend of the tube, and gas bubbles begin to come off more briskly. Test the gas which bubbles up through the water in the pneumatic trough by bringing a glowing chip of wood near it. If the latter bursts into flame, this is due to the gas which comes off from the red powder, as air would not inflame it. A glass cylinder, full of water, is then inverted over the mouth of the delivery-tube, and some of the gas collected. The cylinder becomes gradually filled with a colourless invisible gas. The metallic mirror in the bend of the tube increases, and collects in heavy drops. This liquid metal is mercury. When the whole of the red powder has been volatilized, and converted by heat into a gas and a liquid metal, the lamp is removed, and the delivery-tube taken out of the water. The condensed mercury may now be weighed in a little counterpoised porcelain dish. It weighs less than the red powder employed. Something, then, has been removed from the latter, viz., the gas collected in the cylinder.

If the experiment be conducted with proper care, and in a perfectly suitable apparatus, it will be found that 100 parts by weight of the red powder leave invariably 92.59 of metallic mercury, or in the proportion of 216 : 200, and consequently yield 16 parts by weight of oxygen gas from every 216 parts of the red powder. The latter is a compound of mercury and oxygen, and is called mercuric oxide.

*What is this gas, and what are its properties?*

By closing the cylinder with a small glass plate, the gas can be removed without loss, and on introducing a glowing taper or ignited chip of wood into it, the taper or wood bursts into flame (Fig. 13), and burns very brilliantly.

*This gas, therefore, supports combustion much more readily than the air from which it was originally derived (comp. Exp. 7). It is*

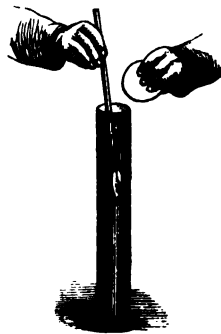


FIG. 13.

called *oxygen*, or acid producer, from *ὀξύς*, sour, acid, and *γεννάω*, I generate (because chemists thought, at one time, that oxygen entered into the composition of every acid), and the symbol O has been assigned to it.

The metal mercury, symbol Hg, from *hydrargyrum*, by combining with the gas oxygen forms an *oxide*, mercuric oxide (red precipitate), and the symbol HgO is used to express its composition.



FIG. 14. — PREPARATION OF NITROGEN.

**Experiment 9.**—Introduce a small piece of phosphorus, dried between filter paper, into a porcelain crucible, which floats on water, as seen in Fig. 14. Set fire to the phosphorus, and rapidly invert an empty bell-jar over the burning phosphorus, so that the combustion can only take place at the expense of the air confined over water under the bell-jar. The latter becomes filled with dense white fumes, which gradually sink down, and are absorbed by the water. A diminution of about one-fifth in the volume of the air takes place, and in proportion as the air disappears, the water rises in the bell-jar. As soon as the combustion has ceased, the crucible may be removed from beneath the glass vessel. By slipping a glass plate over the mouth of the jar, it can be readily removed, and its contents examined. This is done by introducing a lighted taper into the colourless gas left in the bell-jar. The burning taper is immediately extinguished.

The gas, therefore, *no longer supports combustion. It is no longer air.* The phosphorus possessed a strong affinity for that constituent of the air, which is alone capable of supporting combustion, viz., the oxygen, an affinity which is greater than that which the metal mercury exhibited in Experiment 7. The air must, therefore, be a mixture\* of a gas which supports combustion, viz., oxygen and another gas which does not sustain combustion. This latter has been called *nitrogen*, i.e., generator of nitre, also *azote* (from a privative, and *ζωτικός*, belonging to life), and is represented briefly by the symbol N.

Air, according to this approximate determination, consists of about one volume of oxygen and four volumes of nitrogen. Exact experiments have shown that air contains:—

	By volume.	By weight.
Oxygen .....	20.9	23.2
Nitrogen .....	79.1	76.8
	<hr/> 100.0	<hr/> 100.0

These proportions of oxygen and nitrogen in air have, moreover, been found to vary but little all over our globe.

The specific gravity of oxygen and nitrogen is readily deduced from these numbers, viz.,  $\frac{23.2}{20.9} = 1.1$ , and  $\frac{76.8}{79.1} = .97$ .

\* When a mixture of nitrogen and oxygen, in the proportions in which they are present in air, is made, no chemical combination takes place between the two gases. The mixture has all the properties of atmospheric air.

Air contains, besides these two constituents, a small proportion of a gas called carbonic anhydride,\* and more or less vapour of water.

The porcelain crucible generally contains some remnants of unburnt phosphorus, which should be kept covered with water, as the affinity which phosphorus possesses for oxygen is so great that it cannot be kept in air, and great care ought to be taken to prevent spontaneous inflammation whilst operating with it. Phosphorus should, therefore, not be touched with the fingers, but should be taken out of the water with a pointed knife, or a pair of crucible-tongs, and cut into small pieces of the size of a pea under water.

The white fumes, or the product of the combustion of phosphorus in air, called *phosphoric anhydride*, will be explained more fully hereafter.

**Experiment 10.**—Expose a few thin strips of bright metallic sodium to the air in a flat porcelain dish. The metal tarnishes rapidly, and becomes coated with a dirty white layer of oxide, by abstracting oxygen from the atmosphere. The metal sodium oxidizes, in fact, slowly in air. The crust of oxide attracts moisture from the air, and speedily deliquesces. Thick pieces of metal on becoming coated over with oxide thereby become protected from the further action of dry air. On removing the layers of oxide and dissolving them in a little distilled water, a clear liquid is obtained, which feels greasy to the touch, tastes very caustic, and turns *red litmus-paper blue*,† i.e., it has an alkaline reaction.

The powder is in fact an oxide of sodium, or *soda*, also called *caustic soda*, and *sodic hydrate*. The symbol for sodium is Na; from *Natrium*, the name given to the metal by German chemists.

Instead of the metal sodium we might have employed the metal potassium with similar results. An oxide of potassium, or potassa (potassic hydrate), would have been left in the dish. The symbol for potassium is K (from *Kalium*).

On account of the great attraction which these metals possess for oxygen, they have to be carefully kept in a liquid which does not contain oxygen, viz., petroleum. Sodium being so much cheaper and less oxidizable than potassium, is now almost invariably used, since it exhibits similar properties, only in a less marked degree. Sodium may be cut with a knife, and can be handled with dry fingers, without danger of its bursting into flame from too rapid oxidation. The oxides of both metals attract moisture from the air most eagerly, and are gradually converted into thick oily liquids containing sodic and potassic hydrates.

**Experiment 11.**—We are acquainted with other metals which are acted

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\* The term anhydride is applied to oxides which form acids by combining with water, or salts, when added to a base. It will be explained more fully in a subsequent chapter.

† Litmus, a vegetable colouring matter found in many lichens, is employed for preparing test-papers. The blue colouring matter is easily extracted by water from the litmus sold in commerce—six parts of water to one part of litmus—or very dilute solution of ammonia. Sheets of unsized paper are dipped into the filtered solution and dried. To produce red litmus-paper, the aqueous solution of the colouring matter is first turned red by the addition of a few drops of very dilute sulphuric acid.

upon by atmospheric air. A piece of magnesium wire or foil can be kept in the air without undergoing much change. It tarnishes only slightly.

Hold the metal, however, for a moment in a flame, and it burns most brilliantly, *i.e.*, it deprives the air of one of its constituents—Oxygen, with which it forms an oxide of magnesium or magnesia. Symbol  $MgO$ . The symbol adopted for magnesium being  $Mg$ .

The wire continues to burn after its removal from the flame.

Magnesia is a white earthy-looking powder, which is but little soluble in water, has only a feebly alkaline reaction on red litmus-paper, and little attraction for water. This experiment proves that the metal magnesium has at the ordinary temperature much less affinity for oxygen than either sodium or potassium.

Some metals which volatilize at a high temperature burn vividly, and with a flame, *i.e.*, in the finely divided condition of vapour they combine readily with the oxygen of the air.

**Experiment 12.**—Heat metallic zinc in a porcelain crucible over a gas flame (Fig. 15). It melts and becomes coated over with an iridescent film of oxide. On raising the temperature the metal volatilizes, and its fumes burst into a dazzling bluish-white flame, giving rise to white smoke of zincic oxide. Thin sheet-zinc burns in a Bunsen flame as fast as it melts. The oxide may be collected. It is not soluble in water, and shows no action upon litmus-paper.

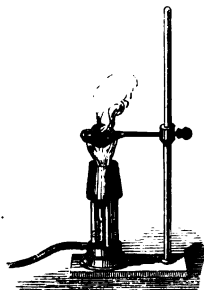


FIG. 15.—COMBUSTION OF ZINC IN AIR.

The symbol for zinc is  $Zn$ , and for zincic oxide,  $ZnO$ .

**Experiment 13.**—A piece of thin steel wire, when kept in dry air, remains bright and unchanged. On raising the temperature of the wire to intense white heat, by holding it in the flame of a gas-burner, it begins to burn, and to cast off brilliant sparks, *i.e.*, the metal iron (steel is almost pure iron) combines with the oxygen of the air at a white heat, and forms with it an iron oxide resembling the black iron scales that fall

from a smith's anvil when a hot piece of iron is hammered out. On removing the steel wire from the gas flame, however, the combustion ceases immediately.

The symbol for this iron oxide is  $Fe_3O_4$ , the symbol for iron being  $Fe$ , from *Ferrum*. This oxide is not soluble in water, shows no alkaline reaction (in fact no reaction at all) with red litmus-paper, and is only slowly affected by water in the presence of air and carbonic acid, being converted into iron rust.

These experiments prove, then, that the metal iron has less affinity for atmospheric oxygen than either sodium, magnesium, or zinc.

**Experiment 14.**—Heat a piece of lead in an iron spoon over a gas-burner; the metal melts, the surface of the molten metal is at first bright, then becomes covered with a yellowish film.

The oxygen of the air by combining with the lead, forms lead oxide, or plumbic oxide (from *Plumbum* lead, symbol  $Pb$ ), the symbol of which is  $PbO$ . It is insoluble in water, and has no action on litmus-paper.

**Experiment 15.**—Heat some bright copper turnings in a gas flame; they become rapidly covered with a black film of copper or cupric oxide,  $CuO$  (from

*Cuprum*, symbol Cu), which peels off readily (copper scales), and is obtained as a black powder, insoluble in water, having no action upon litmus-papers.

The action of atmospheric air upon the metal copper may be illustrated further by a simple experiment, showing conclusively that only one constituent of the air, viz., its oxygen, is capable of combining with the copper to form the black oxide of that metal.

**Experiment 16.**—Fill a glass combustion tube, *e f*, with bright copper turnings, and heat the tube in a small charcoal (or, if procurable, gas) furnace (Fig. 16).

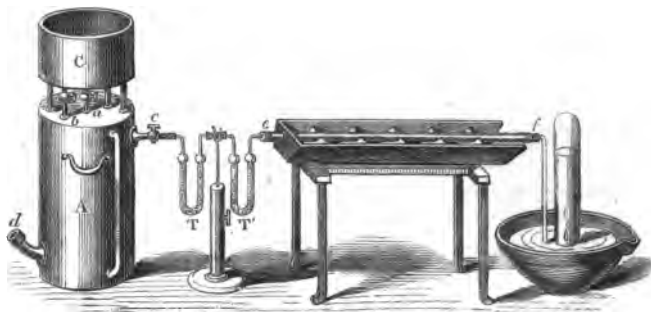


FIG. 16.—OXIDATION OF COPPER IN AIR.

Pass a current of air from the gasholder, A. The air is made to pass through two U-tubes, T and T', before it enters the combustion-tube at *e*. The first U-tube contains small pieces of pumice-stone moistened with a solution of caustic potash, which absorbs the traces of carbonic anhydride contained in the air. The second U-tube contains pumice-stone saturated with concentrated sulphuric acid,\* which possesses a powerful attraction for water, and retains every trace of moisture which the air carries along with it. Connect a delivery-tube with the end, *f*, of the combustion-tube, for the purpose of collecting the gas which passes off over a pneumatic trough, as seen in Fig. 16.

Pass air over the copper without applying heat to the tube. No action takes place, the copper retains its metallic lustre. Collect some of the air in a glass cylinder over water and introduce a lighted taper. The taper continues to burn quietly. Heat the copper next to bright redness by heaping ignited charcoal all round the combustion-tube. The metallic copper remains unchanged. Now turn on a slow current of air, and the metal is seen to blacken from the anterior end of the layer of copper turnings onwards. Collect the gas, which issues from the delivery-tube under water, in a glass cylinder, and test it again by inserting a lighted taper: it no longer supports combustion, for the taper is extinguished.

*The gas is no longer air, it is in fact nitrogen gas.*

This constitutes, then, a ready method of obtaining pure nitrogen gas. When thus obtained it is a colourless, tasteless, and odourless gas. It is a non-supporter of animal life without, however, being directly poisonous, for we inhale it constantly in atmospheric air, in which it moderates the action of the oxygen. Water dissolves nitrogen only to the extent of about one-fiftieth of its own bulk. Nitrogen has never been liquefied by cold or pressure. It is slightly

\* The pumice-stone and sulphuric acid are heated together for a short time in a porcelain dish, and the excess of acid drained off before the U-tube is filled.



lighter than air, its specific gravity, compared with that of air, being .971, or 14, as compared with hydrogen.

Pass air till the whole of the metallic copper has been converted into the black oxide, which can readily be ascertained by collecting from time to time some of the gas over water, and testing it with a lighted taper. The oxidation is finished as soon as the gas supports once more the combustion of the taper.

By weighing the copper turnings previous to their introduction into the combustion-tube, and weighing again after complete oxidation has been effected, we find an increase in weight. The copper, like the metal mercury in Exp. 7, has attracted some ponderable matter from the air. The increase in weight remains proportionally the same, however frequently the experiment may be repeated. The weight of the metallic copper to that of oxide is as 100 : 125.2, or (for reasons to be explained hereafter) in the proportion of 63.5 of copper to 79.5 of oxide, i.e., 63.5 parts by weight of metal combine with 16 parts by weight of oxygen.

**Experiment 17.**—Heat gold or platinum wire, or foil, in a Bunsen gas flame. Neither of these metals is affected by the oxygen of the air.

Gold and platinum exhibit, under these circumstances, no affinity for oxygen.

**Summary.**—*Some metals can take Oxygen from the air and form Oxides. Combustion and oxidation are, chemically speaking, the same operation. Combustion in air or oxygen does not imply destruction, but merely conversion of the combustible substance into a new body, into an Oxide.*

*Some metals possess a great affinity for Oxygen, and form Oxides readily; other metals combine with Oxygen only at a high temperature; others, again, do not combine directly with Oxygen at all, possessing but a very feeble affinity for that element. These latter metals are sometimes called noble metals.*

*Atmospheric air consists mainly of two gases, of Oxygen and Nitrogen, in the proportion of about one-fifth to four-fifths by volume. Oxygen sustains combustion and animal life. Nitrogen is a non-supporter of combustion, and cannot sustain animal life.*

#### *Properties of Oxygen.*

Experiment 7 has shown that oxygen can be removed from atmospheric air, and obtained in a pure state. It would, however, be both expensive and tedious to obtain large quantities of oxygen by the method described. We avail ourselves in the laboratory, therefore, of the property which a certain salt, called *potassic chlorate*, possesses, of readily parting with its oxygen when heated, leaving another salt, which does not contain oxygen, viz., *potassic chloride*. This salt is as yet of interest to us only as a convenient source of oxygen.

**Experiment 18.**—Heat in a Florence flask or test-tube (Fig. 17) a few grammes of potassic chlorate,  $\text{KClO}_3$ . Collect the gas over water by means of test-tubes, or cylinders. By first powdering the salt, and then mixing a small

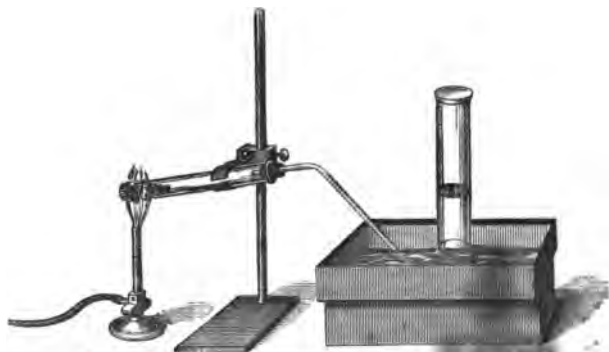


FIG. 17.—PREPARATION OF OXYGEN FROM POTASSIC CHLORATE.

quantity of red oxide of iron (iron rust) or black oxide of manganese with the powder, and heating such mixture in the flask, or test-tube, a far more ready evolution of oxygen is effected than by heating the salt by itself.

For the purpose of collecting a larger volume of gas, sufficient for several experiments, it is preferable to employ a gasholder, as shown in Fig. 18.

In order to examine the gas, it will be found most convenient to first transfer a portion from the gasholder to wide-necked glass bottles, closed by means of a cork. The bottles are completely filled under water, in the vessel B of the gas-holder (Fig. 18). On placing them over the central tube, which connects the lower vessel A of the gasholder with the upper water reservoir B, and opening first the

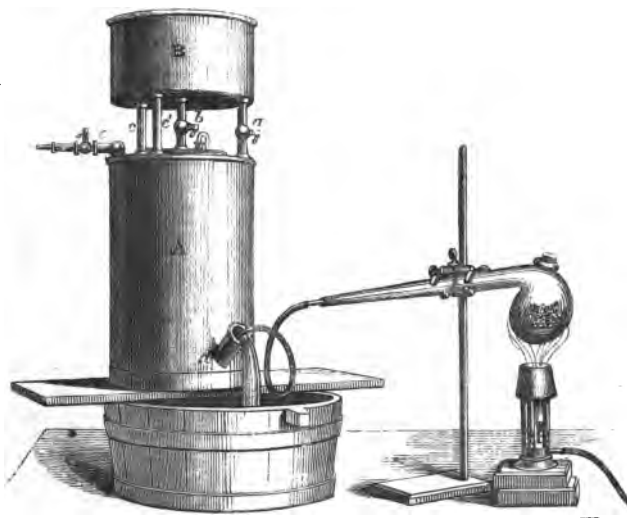
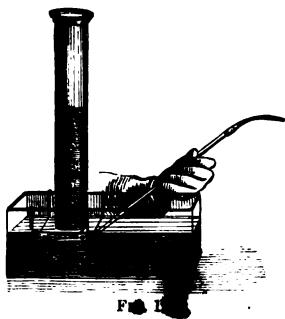


FIG. 18.—PREPARATION OF OXYGEN.

stopcock at *a*, which allows the water to flow from B to the bottom of the vessel A, and then the stopcock at *b*, the column of water in B forces the gas rapidly into the bottles.



In the absence of a gasholder, the gas may be directly filled into the glass bottle or cylinder, from the evolution flask or retort (Fig. 19).

The bottles containing the oxygen are then removed from the water. For this purpose their wide mouth is closed under water by means of a cork, and their contents can now be examined at pleasure.

**Experiment 19.**—Heat a piece of magnesium wire in a gas flame, till it bursts into flame. Introduce it rapidly into a bottle filled with oxygen; the combustion becomes of a most dazzling brilliancy, and the resulting white oxide (magnesia) is identical with the white powder obtained on burning magnesium in the air (comp. Exp. 11).

**Experiment 20.**—Zinc turnings, slightly dipped into sulphur, burn on ignition of the sulphur with a dazzling white light, when plunged into a bottle containing oxygen. The result of the combustion is the same as in Exp. 12, viz., zinc oxide.

Oxygen is capable of combining with all elementary bodies, except fluorine.

Substances which burn readily in the air, burn with still greater energy in oxygen gas; this may be illustrated further by the following experiments.

**Experiment 21.**—A thin watch-spring is fastened to a cork, which fits loosely into the mouth of a wide-necked bottle, Fig. 20. The steel spring must be heated first, before it can be coiled up into a spiral form. In order to cause the oxygen in the bottle to act upon the iron of the watch-spring, the temperature of the latter must be raised by fastening to the end of the watch-spring a piece



FIG. 20.



FIG. 21.

of tinder or dry charcoal. The tinder or charcoal is ignited, the cork which closes the bottle is removed, and the cork with the watch-spring rapidly inserted. The tinder or charcoal, which at first only glows, burns vividly, and quickly raises the temperature of the watch-spring, till the latter burns likewise, and gives a most dazzling light, throwing off sparks of melted metal and of oxide, which fall with a hissing noise into the water left in the bottle, in order to prevent the globules of molten iron from breaking the glass.

This experiment proves that iron, which in the form of thin wire

can be burnt in air, by holding it in a gas flame, burns in free oxygen with great brilliancy, and gives off much heat. The product of its combustion in oxygen is the *iron oxide*  $\text{Fe}_3\text{O}_4$ .

**Experiment 22.**—Another bottle (Fig. 21) is filled in a similar manner with oxygen. A wooden cover is fitted to its mouth, through which passes a stout wire, to the lower end of which a small iron spoon—a so-called deflagrating spoon—is fastened. A few pieces of sulphur are placed in the spoon, and inflamed previous to their introduction into the oxygen gas. The sulphur burns in the air slowly, with a pale blue flame. As soon as the ignited sulphur comes in contact with the oxygen of the bottle, it burns brilliantly, with a dazzling blue flame. On examining the bottle after the combustion is over, a suffocating gas is found to be left, having the odour of burning matches. Introduce a piece of blue litmus-paper into the gas. It is turned red instantaneously. On introducing a lighted taper, the light is immediately extinguished. The gas does not support combustion.

This gas has received the name *sulphur dioxide* or *sulphurous anhydride* ( $\text{SO}_2$ ).

**Experiment 23.**—Fill another bottle with oxygen, and introduce in like manner a piece of phosphorus, another elementary body, as we have already seen, which possesses a great affinity for oxygen. The small piece of phosphorus to be employed is dried rapidly between folds of filter-paper, and then placed in the iron spoon, ignited, and rapidly introduced into the bottle. Phosphorus burns with most intense light in oxygen gas, producing at the same time great heat. Should any of the burning phosphorus be spurted from the iron spoon, and come in contact with the glass, it will cause the glass to crack, without doing, however, any further harm. The whole bottle is filled with clouds of a heavy white compound, which gradually subside. On letting it stand for a little while, these white clouds disappear. They combine with the water, with which they form an acid substance. Test the water with litmus-paper; it turns blue litmus red. The liquid possesses an acid taste.

The white compound formed by the combustion of phosphorus in oxygen gas is called *phosphorus pentoxide* or *phosphoric anhydride* ( $\text{P}_2\text{O}_5$ ). The product of the action of water upon this compound is called *phosphoric acid*.

**Experiment 24.**—Arrange apparatus in such a manner as to pass a current of oxygen gas from the delivery-tube of the gasholder over pieces of ignited charcoal placed in a piece of combustion-tube, connected by means of corks and india-rubber tubing into a glass cylinder, as shown in Fig. 22. Previous to applying heat to the charcoal, and before turning on the oxygen gas from *e*, introduce a lighted taper into the glass cylinder.

It continues to burn. Apply heat to the tube where the charcoal rests; it begins to glow. Now pass a *slow* current of oxygen gas, the charcoal immediately burns most vividly, and the combustion goes on *without any external application of heat*.

When the combustion has proceeded a few minutes, introduce the lighted taper again into the glass cylinder which received the gaseous product of combustion. The light of the taper is extinguished. The gas in the cylinder is neither air nor oxygen. A series of burning tapers fixed on wires at various heights may also be introduced into a second wider cylinder. The taper placed lowest will be extinguished first, then the next above it, and so on, till all are extinguished. The charcoal in the combustion tube is gradually consumed and carried away as gas.

It burns at the expense of the oxygen, *i.e.*, it combines with the latter and forms an oxide of carbon, called *carbon dioxide* or *carbonic anhydride* ( $\text{CO}_2$ ).

This experiment proves then clearly that the colourless gas which results from the combustion of carbon in oxygen *does not support combustion*.

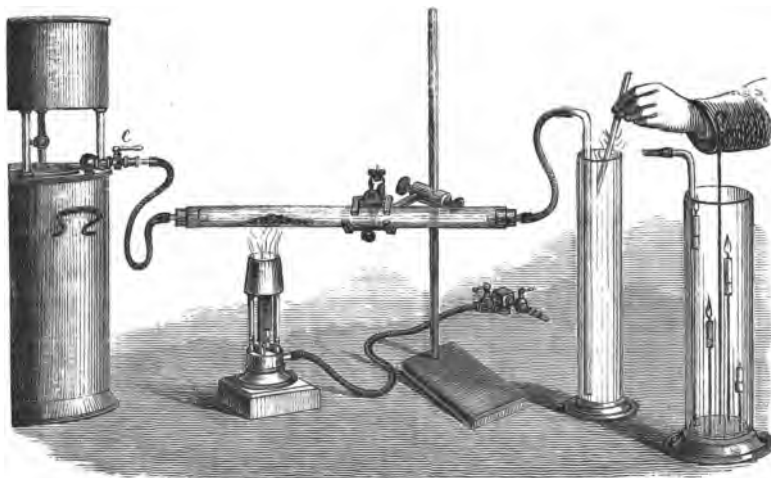


FIG. 22.—COMBUSTION OF CARBON IN OXYGEN.

Combustion, in the sense used to express this and some of the preceding chemical changes, is accompanied by the phenomenon of light and the evolution of heat. The body to be burnt requires to be heated first to the initial temperature at which a chemical change can take place; sufficient heat is afterwards given out to keep up the combustion, and to carry it on—provided a free supply of oxygen or air can be obtained—till the body is consumed, *i.e.*, altered in form, as in Experiment 24, when the solid carbon vanished gradually and was converted into the gaseous body carbonic anhydride. An analogous instance we have in the case of an ordinary coal fire burning in a fire-grate. The amount of heat actually produced by a given weight of carbon, no matter whether burnt quickly, in oxygen, or slowly, in air, is the same. The sensible heat, however, was greater in our experiment, because there was no nitrogen to dilute the oxygen, as when carbon is burnt in atmospheric air, and when the non-combustible nitrogen has to be raised to the temperature of the flame, without itself contributing any heat to the combustion. Consequently the more the oxygen—the element which supports combustion—is diluted, the less energetic becomes the combustion. The charcoal in the glass tube burnt more or less energetically, in proportion as the admission of oxygen from the gas-holder was increased or decreased. A coal fire is quickened by forcing air into it by a pair of bellows; not only is fresh air supplied more rapidly, but the chief product of the combustion, carbonic anhydride, which is a non-supporter of combustion, is carried away more rapidly. A

good chimney draught accomplishes the same. Compressed air, as used to feed blast-furnaces, acts for like reasons more energetically than ordinary air. Combustion is accompanied by flame only in the case of bodies which are converted into vapour previous to their burning. Instances: steel wire and coke, compared with zinc, sulphur, phosphorus, or bituminous coal, all of which are volatilized before they burn with a luminous flame.

**Experiment 25.**—Collect some carbonic anhydride in a cylinder over warm water in a pneumatic trough. Remove the cylinder when full of gas by closing it with a glass plate. Pour the gas into another cylinder in which a small burning taper is placed, Fig. 23. The taper is extinguished, and it can be clearly seen how the carbonic anhydride by falling through the air of the upright cylinder, at first forces down the flame, till at last it entirely extinguishes it.

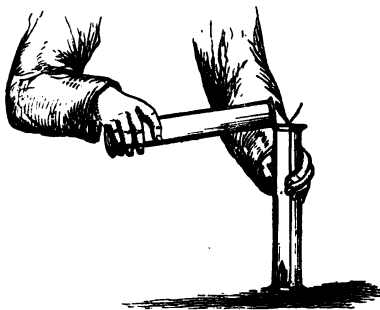


FIG. 23.

This proves that carbonic anhydride is *heavier than air*, and that it consequently falls through the air.

**Experiment 26.**—In like manner fill a stoppered glass cylinder with carbonic anhydride, close the mouth with the ground glass stopper under water, and remove the cylinder to a trough containing *cold*, but recently boiled water. Open the cylinder under water. The water rises slowly, the gas being absorbed by the water. This absorption may be accelerated by vigorously shaking. The water now tastes slightly *acid*, and a strip of blue litmus-paper is slightly reddened.

This proves that *carbonic anhydride is absorbed by water, and that its solution is a weak acid*, which is called *carbonic acid*. Heat expels it again. Natural waters contain carbonic acid.

**Experiment 27.**—Pass the carbonic anhydride generated by the combustion of charcoal in oxygen from the combustion-tube, directly into a test-tube containing lime-water (*i.e.*, a clear solution of slaked lime in water). The first bubbles cause a milkiness, and in a few minutes a quantity of a heavy white powder is formed, which on interrupting the current of gas, gradually falls to the bottom of the test-tube. This powder is evidently the result of the action of the gas upon the lime dissolved in the water. If the gas is passed somewhat longer, the white powder gradually dissolves again. This proves that the latter is soluble in excess of carbonic acid. On adding lime-water, the clear liquid becomes once more milky. The same happens when heat is applied. In the latter case some of the gas is seen to come off.

It has been already shown that water is formed by the combustion of hydrogen in air, and that a mixture of hydrogen and air, when ignited, explodes with great violence and forms water. A mixture of hydrogen and oxygen gas explodes with still greater violence, especially if the mixture consists of one volume of oxygen to two volumes of hydrogen.

The heat produced by the combustion of oxygen and hydrogen is

## 18 VOLUME COMBINATION OF HYDROGEN AND OXYGEN.

very great. A jet of oxygen directed into a flame of hydrogen causes sufficient heat to melt a platinum wire.

**Experiment 28.**—Soak a good sized bladder in water till it is quite soft. Insert into the neck of the bladder V a tube provided with a stop-cock *r*, shown in Fig. 24. A tubulated bell-jar is fitted with a stop-cock *s*. By plunging the jar C into the water contained in the upper vessel B of the gasholder, it can be filled entirely with water by simply opening the stopcock at *s*, and allowing the air to escape. The stopcock is then shut off and the bell-jar connected with the tube of the empty bladder by means of a piece of india-rubber tubing.

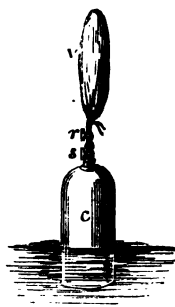


FIG. 24.

The bell-jar is next filled with oxygen, as described under Experiment 18. By opening the stopcocks *s* and *r*, the gas is transferred to the bladder V.

By filling and discharging in like manner the same bell-jar twice with hydrogen gas from another gasholder filled with hydrogen, the bladder can be charged with a mixture of one part by volume of oxygen, and two parts by volume of hydrogen. According to a beautiful law of nature, the two gases rapidly diffuse and intermingle most intimately, and the gaseous contents of the bladder now constitute a highly explosive mixture, the explosive nature of which may be shown by filling soap-bubbles with the gas. A solution

of soap and glycerine is most suitable for this purpose. The cup at the upper end of the tube which delivers the gas from the bladder, is dipped into the soap-solution. The stopcock is then opened, and, by applying a gentle pressure to the bladder, a bubble can be blown and shaken off by a slight side-movement of the tube. The bubble ascends rapidly, because the gaseous mixture with which it is charged is lighter than air, and can be exploded by applying a light to it as it ascends. Each bubble bursts with a sharp report.

If no gasholders are at the operator's disposal the two gases may also be filled in the proper proportions, one after another, directly from the generating flask and retort into the bell-jar, which for this purpose is divided into three equal parts, and is placed full of water over a pneumatic trough.

This experiment shows that hydrogen and oxygen do not combine at the ordinary temperature, but if the temperature of a very small portion of their mixture be raised by applying a light to it, the heat which is produced by the chemical combination of hydrogen and oxygen communicates itself with great rapidity to the rest, and the whole mixture explodes. Water is formed by the combination of two volumes of hydrogen and one volume of oxygen.

The combination of hydrogen and oxygen in these proportions can be shown in many other ways, but the highly explosive nature of the mixture renders it advisable for the operator not to attempt at first any more elaborate experiments.

Some of the elementary bodies hitherto treated of possess properties which appertain only to *metals*, others again lack such properties entirely, *e.g.*, carbon, sulphur, phosphorus. These latter bodies are called *non-metals* or *metalloids*.\* Some of the elementary

\* From *μέταλλον*, metal, and *είδος*, form. It is difficult to draw the line of demarcation between metals and metalloids very sharply. *Metals* are opaque bodies, having a peculiar lustre, known as *metallic lustre*, and are good conductors of heat and electricity. *Metalloids* do not possess these properties in the same degree.

gases already examined, viz., oxygen, hydrogen, nitrogen, belong likewise to the non-metals.

**Summary.**—*Pure oxygen combines energetically with metallic as well as non-metallic elements. Oxygen mixed with nitrogen, as in air, combines less energetically. The nitrogen acts as a diluent.*

*Heat is produced by the combination of oxygen with other elementary bodies. Such combination is frequently accompanied by the phenomenon of light.*

*The oxides of metallic bodies are solid bodies, either soluble in water and of a caustic or alkaline nature, or insoluble in water. They are also called bases.*

*The oxides of non-metallic bodies are either gaseous, liquid, or solid bodies. They dissolve for the most part in water, and many possess acid properties.*

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### CHAPTER III.

## PHYSICAL STATE OF MATTER. MECHANICAL MIXTURE. CHEMICAL REACTIONS (Combinations and Decompositions). ELEMENTS.

THE physical condition of everything around us, no matter whether of a simple or compound nature, depends mainly upon temperature. Water is a liquid body at the ordinary temperature. If the temperature fall below 0° Centigrade (32° Fahrenheit) this liquid solidifies and becomes *ice*.\* Again, if the temperature of the water be raised by the application of heat, the liquid becomes converted into water vapour, or *steam*. It forms then a clear, transparent, colourless gas, devoid of smell or taste. That temperature is indicated on the thermometer scale at 100° Centigrade (212° Fahrenheit) at the ordinary atmospheric pressure. Water remains *unchanged in composition*, i.e., it is still composed of hydrogen and oxygen, in the proportion by volume of two to one respectively, whether it exist in the solid, liquid, or gaseous form, as ice, water, or steam. It merely changes its state of aggregation, and this change is dependent upon a loss or gain of heat alone. It is a mere *physical change*.

Most simple bodies occur at the ordinary temperature and pressure of our atmosphere as *solids*; two only, viz., mercury (quick-silver) and bromine exist as *liquids*, but solidify respectively at -40° C. and -24.5° C. Four are known as *gases*, viz., hydrogen, oxygen, nitrogen, and chlorine, the last only being condensable by great cold and pressure; all others are solids. Many solids may

\* Water may be cooled to -12° C. without freezing, if it be left perfectly undisturbed.



either be converted into liquids and gases by raising the temperature, as *e.g.*, the metal zinc (compare Exp. 12); or reversely, gaseous bodies into liquids and solids by lowering the temperature.

All solid elementary bodies, with the sole exception of carbon, have been melted or liquefied, though some of them require a very high degree of heat, such as the metal platinum. The alteration in their physical condition does not affect their weight. Solid elementary bodies which cannot be liquefied or volatilized by the heat of our ordinary furnaces, melt and vaporize readily when exposed to the extreme heat of the voltaic arc or the electric current produced between the poles of a powerful voltaic battery. Liquid bodies contract on passing from the fluid to the solid form. Water forms a remarkable exception. It reaches its maximum density at  $4^{\circ}\text{C}$ ., and below that temperature it gradually expands again till it reaches the freezing point  $0^{\circ}\text{C}$ ., when, as ice, it suddenly expands still more. Ice, therefore, floats upon the surface of our rivers and lakes, its density or specific gravity being  $\cdot 918$  compared with  $1\cdot 00$ , the sp. gr. of water at  $4^{\circ}$ .<sup>\*</sup> The temperature of the water below remains constant. Animals living in ice-bound waters are thus protected from the most severe winter frosts.

Solid and liquid bodies alter their bulk but slightly by heat or cold, or by compression; gases, on the other hand, are elastic bodies, which can be visibly compressed, and which contract or expand at a given constant ratio by cold or heat. By the united action of cold and pressure, most gases are reduced to the liquid state, some even to the solid condition; a few gases only, among which are oxygen, hydrogen, and nitrogen, have never been liquefied, although there

\* The density of liquids, as well as solids, is measured by taking the density of water at  $4^{\circ}\text{C}$ . as the standard unit. One litre of water at  $4^{\circ}\text{C}$ . weighs exactly 1,000 grammes or 1 kilogramme (about  $2\frac{1}{2}$  lb. English). The advantages which French measures and weights possess will become readily apparent, if we bear in mind that a litre is a cubic decimetre, equivalent to 1,000 cubic centimetres, both these measures being derived from the French unit of length, the metre (equal to  $39\cdot 37$  English inches). The unit of length, the metre, and the unit of capacity, the cubic metre, or, in the simpler forms, the decimetre and the cubic decimetre or litre, or the centimetre and cubic centimetre stand in a simple relation to the unit of weight most frequently used by chemists, viz., the weight of 1 cubic centimetre of distilled water at  $4^{\circ}\text{C}$ ., called a gramme (=  $15\cdot 432$  English grains). To determine the density or specific gravity of a *liquid* body, we have merely to ascertain the weight of a given bulk, say 50 cubic centimetres, at  $4^{\circ}\text{C}$ ., and to divide the weight found by 50 grms., *i.e.*, the weight of the same bulk of distilled water at  $4^{\circ}\text{C}$ . It is usual, however, to weigh the liquid at  $15\cdot 5^{\circ}\text{C}$ . ( $60^{\circ}\text{F}$ .), the process of weighing being thus rendered so much more easy, and to divide the weight by the weight of the same bulk of distilled water at  $15\cdot 5^{\circ}\text{C}$ ., when of course the relative specific gravities remain unchanged.

*Solid* bodies heavier than water displace a certain amount of water; and by ascertaining the weight of the water so displaced, and dividing it into the actual weight of the solid body immersed (which has to be ascertained previously by direct weighing); we arrive at the specific gravity of the solid body. Gold, for example, has been found to displace  $19\cdot 34$  times the weight of its own bulk of distilled water at  $4^{\circ}\text{C}$ ., *i.e.*, it is  $19\cdot 34$  times heavier than the latter, or its specific gravity is  $19\cdot 34$ . Mercury displaces  $13\cdot 59$  times its weight of distilled water at  $4^{\circ}\text{C}$ ; its specific gravity is therefore  $13\cdot 59$ .

can be little doubt that their liquefaction is merely a question of intenser cold and greater pressure than physicists can at present command. Experiment 9 has shown that air is a *mechanical mixture*, mainly of two gases, of oxygen and nitrogen. Nature supplies us with numerous other instances of mere mixtures. Muddy water holding particles of solid matter in suspension yields, on freezing, pure ice, any suspended solid particles being thereby removed. On filtering dirty water through a little white sand or filtering-paper, the water becomes clear, the solid ingredients being left on the filter.

**Experiment 29.**—Place a little ordinary gunpowder on a filter and wash it with warm distilled water. It leaves a black residue on the filter, which, when dried, no longer deflagrates like powder, but burns with a bluish flame, giving off the pungent odour of burning sulphur. On evaporating the clear filtrate in a small porcelain dish over a spirit lamp, or a small gas flame, a white crystalline salt is left, known as nitre. If the residue on the filter be thoroughly dried, by placing the filter in a warm place, and then treated in a test-tube or flask with a little carbonic disulphide, heated by placing the test-tube into some warm water, and the extraction repeated several times with small quantities of the disulphide, we obtain at last on the filter a black carbonous residue, which on drying in a warm place and ignition no longer burns with a bluish flame, nor emits the odour of burning sulphur. This residue consists now only of finely divided charcoal. By placing the carbonic disulphide liquid into an evaporating dish over some hot water (without applying a direct flame) near a good chimney draught, a yellow crystalline residue (octahedral crystals) of sulphur (brimstone) is obtained, which on ignition burns with a bluish flame, and gives off the characteristic suffocating odour of burning sulphur.

Now, gunpowder is manufactured by intimately grinding together in a moist condition finely divided charcoal, nitre, and flowers of sulphur. The moist mass is strongly compressed, formed into grains, and then cautiously dried. However carefully the ingredients may have been ground together, they will always remain only mechanically combined, for we have seen that the two soluble bodies, the nitre and the sulphur, the first soluble in water and the second in carbonic disulphide, can be separated consecutively from the carbon, this latter not being soluble in any known solvent. Gunpowder is in fact a mere *mechanical mixture* of these three solid bodies. But if a spark be allowed to fall upon a little gunpowder, it is converted with a sudden flash mainly into gaseous bodies, which become diffused into the surrounding atmosphere, or which, when confined in a gun barrel, can be made to drive a bullet with considerable force. The black carbon, the yellow sulphur, and the white salt, the nitre, exist in fact no longer as such, but their elements have entered into fresh combinations, and have formed new bodies, partly gaseous and partly solid, perfectly different in their properties from the ingredients employed in the manufacture of the gunpowder. The change which took place is no longer a mere *physical* change, it is called a *chemical* change.

**Experiment 30.**—Mix about equal parts by weight of fine iron filings and flowers of sulphur in a mortar. Shake a portion out on a sheet of white paper, and bring a magnet near the mixture; the iron filings are attracted by the magnet, and can be almost entirely separated from the sulphur. Heat another portion of the mixture in a tube closed at one end (a test-tube), and powder up the fused mass; the magnet no longer separates the iron from the sulphur. Heat

has in fact effected a *chemical* combination between these two elementary bodies. On treating another portion of the mixture with carbonic disulphide in the manner explained in Exp. 29, sulphur is dissolved out, and the iron filings are left behind. On treating in like manner the fused compound of sulphur and iron, or a little of the natural compound (known as iron pyrites), no sulphur is separated.

Mere *mechanical mixture* is therefore readily distinguishable from *chemical combination*.

Heat is mainly employed by the chemist to induce chemical changes, to combine elementary substances, and to break up compound bodies.

A piece of platinum wire when heated in a flame remains unchanged (Exp. 17). A piece of magnesium wire similarly treated bursts into flame (Exp. 19). A piece of dry phosphorus, when exposed to the air, emits white fumes; it undergoes slow oxidation. On placing, however, a red-hot bar of iron at a distance of several inches even, the phosphorus ignites and burns with a brilliant flame. A mixture of sugar and potassic chlorate is unaffected by holding a glass rod dipped into oil of vitriol over it, but inflames as soon as the acid is dropped on it, owing to the heat produced by the chemical action.

We have become acquainted with some changes produced by heat alone, and shall have occasion hereafter to examine many more. Chemical study, to a large extent, consists in fact in combining elementary matter, whereby new compounds are obtained, totally differing for the most part in their properties from those of the separate elements, as well as from the mere mixture of the elements before they were chemically combined.

Many elementary or compound substances cannot be mixed together without inducing at once a change. The metal sodium in Experiment 1, on being brought into contact with water, decomposed it rapidly. Hydrogen gas was evolved, and the oxygen went to the metal sodium, and formed with it a new body, soda, or an oxide of sodium, differing essentially in its properties from the metal itself. *A new body was formed, viz., soda, by the combination of two distinctly different bodies: the sodium, in fact, entered into chemical combination with the oxygen.*

In Experiment 8, we saw that red oxide of mercury, when heated, gave off oxygen gas and mercury. *One uniformly constituted body thus broke up under the influence of heat into two new bodies, differing entirely from each other.* The chemical change arose from the breaking up of one body into two. It was a *chemical decomposition* of a compound body into its constituent parts. Chemistry deals thus with *simple* bodies and *compound* bodies. A compound body which consists only of two simple bodies, is called a *binary* compound.

Water is a binary compound, and so are the metallic oxides called *bases*, e.g., cupric, ferric, plumbic oxides. The names of binary compounds are constructed by using the names of the metallic element adjectively with a terminal *ic*, and giving to the non-metallic element the terminal *ide*. Carbonic anhydride is a binary compound,

for Experiment 24 has shown that it is the result or *product* of the combination of the element carbon with the element oxygen. All combinations of oxygen, either with metals or non-metals, are called *oxides*, and the chemical change which gives rise to the formation of oxides, is called *oxidation*. Since at least two substances are required to produce a new body, the one acting or reacting upon the other, such chemical changes are also called *reactions*, and the bodies which act or react chemically are termed *reagents*.

By way of chemical *decomposition* simpler substances are obtained from compound bodies, as in the case of red oxide of mercury, yielding oxygen and mercury. Metals and metalloids are always simpler bodies than their oxides (bases, acids). The question naturally arises, what are the simple bodies which constitute these metals and metalloids? The answer must be, that it has hitherto been found impossible to decompose these bodies into simpler substances. Such substances, then, which cannot by any known process of decomposition in the present state of chemical knowledge be split up or decomposed into still simpler bodies, must be taken to constitute *absolutely simple* bodies. It does not, however, follow that at some future time means and ways may not be discovered, whereby these metals and non-metals may be decomposed into still simpler bodies. Such absolutely simple bodies for the time being are called *elements*. They form the basis of all chemical compounds.

The endless variety of animate and inanimate forms in nature might at first sight lead us to think that there must be an innumerable host of elements, and that to fathom them all in their manifold and varying characters must be all but impossible to the human mind. Does it not strike us, for instance, that the infinite varieties of form, colour, odour, taste, &c., which constitute the main portion of our experience as regards matter, must be due to an equally varied number of elementary constituents? And yet there are but a few elements which, by combination with each other, make up all the objects that surround us in nature—from the wonders that lie hidden beneath the surface of the earth, even to the very glories of the distant star world above. Although we are as yet very far from knowing every chemical compound that exists in nature, it may safely be stated that no element of any importance has escaped the searching eye of the chemist in that portion of our globe which is accessible to chemical investigation.

The result of such investigation has proved that only a limited number of elements exists. Up to the present time we have become acquainted with 62 elements, of which about one-half occur in nature in such small quantities, and so locally, that a limited share of usefulness only can be ascribed to them in the mineral kingdom, as well as in the economy of animate life. Others again are of the utmost importance, and appear to pervade almost every nook in nature, viz., oxygen, hydrogen, carbon, iron, aluminium, calcium, potassium, sodium. Some of these stand out in truly gigantic proportions, overshadowing all others. We need only refer to oxygen and nitrogen, which form the principal constituents of the mixture of gases,

termed atmospheric air; to oxygen and hydrogen, the constituents of water, and to carbon, the element entering into every organic body, as well as into numerous mineral bodies. Only a few of the elements are met with in nature in the uncombined or native condition, and then only to a limited extent, viz., oxygen and nitrogen in the air, sulphur, carbon (blacklead, diamond), copper, bismuth, mercury, silver, gold, and platinum. Some of the more extensively occurring elements are invariably found in the combined state. The crust of our earth, as far as it has been penetrated and examined, consists to a large extent of oxygen, combined with a comparatively limited number of elements, mainly with silicon, iron, aluminium, calcium, magnesium, potassium, and sodium. The sea, which covers the greater part of our globe, contains, independently of the oxygen and hydrogen of the water, soluble compounds, consisting mainly of the elements sodium, potassium, magnesium, calcium, and chlorine. It will on this account be quite legitimate if a larger share of our attention be bestowed upon the more plentifully occurring elements. In the following table, arranged in alphabetical order, the 36 most important elements are distinguished by black type; those next in importance, 10 in number, by italics; whilst the rest of the elements which occur, either to a very limited extent in nature, or of which we possess as yet a very imperfect knowledge, are printed in small ordinary type. The Latin names—a few of the names are of Greek origin, but have become latinized—are given wherever the English names of elements differ materially therefrom. Chemists have, moreover, adopted a kind of symbolic language by writing merely, as has already been shown, in the place of the full name, the first letter of the Latin name of each element. Sometimes, for the sake of distinguishing between two or more elements beginning with the same letter, the first and second letter, or the first letter together with some leading letter out of the middle of the Latin name are used; thus Sn stands for stannum, tin; Pt stands for platinum; Pb for plumbum, lead; As for arsenic.

TABLE OF CHEMICAL ELEMENTS.

	Symbol.		Symbol.
<b>Aluminium</b> ..	Al.	<b>Copper</b> (Cuprum) ..	Cu.
<b>Antimony</b> (Stibium) ..	Sb.	Didymium ..	Di.
<b>Arsenic</b> ..	As.	<b>Fluorine</b> ..	F.
<b>Barium</b> ..	Ba.	Glucinum ..	Gl.
<b>Bismuth</b> ..	Bi.	<b>Gold</b> (Aurum) ..	Au.
<b>Boron</b> ..	B.	<b>Hydrogen</b> ..	H.
<b>Bromine</b> ..	Br.	Indium ..	In.
<b>Cadmium</b> ..	Cd.	<b>Iodine</b> ..	I.
Caesium ..	Cs.	Iridium ..	Ir.
<b>Calcium</b> ..	Ca.	<b>Iron</b> (Ferrum) ..	Fe.
<b>Carbon</b> ..	C.	Lanthanum ..	La.
Cerium ..	Ce.	<b>Lead</b> (Plumbum) ..	Pb.
<b>Chlorine</b> ..	Cl.	<i>Lithium</i> ..	Li.
<b>Chromium</b> ..	Cr.	<b>Magnesium</b> ..	Mg.
<b>Cobalt</b> ..	Co.	<b>Manganese</b> ..	Mn.

TABLE OF CHEMICAL ELEMENTS (*continued*).

	Symbol.		Symbol.
<b>Mercury</b> (Hydrargyrum) ..	Hg.	<b>Silver</b> (Argentum) ..	Ag.
<b>Molybdenum</b> .. ..	Mo.	<b>Sodium</b> (Natrium) ..	Na.
<b>Nickel</b> .. ..	Ni.	<b>Strontium</b> .. ..	Sr.
<b>Niobium</b> .. ..	Nb.	<b>Sulphur</b> .. ..	S.
<b>Nitrogen</b> .. ..	N.	Tantalum .. ..	Ta.
<b>Osmium</b> .. ..	Os.	Tellurium .. ..	Te.
<b>Oxygen</b> .. ..	O.	<b>Thallium</b> .. ..	Tl.
<b>Palladium</b> .. ..	Pd.	Thorium .. ..	Th.
<b>Phosphorus</b> .. ..	P.	<b>Tin</b> (Stannum) .. ..	Sn.
<b>Platinum</b> .. ..	Pt.	<b>Titanium</b> .. ..	Ti.
<b>Potassium</b> (Kalium) ..	K.	<b>Tungsten</b> (Wolframium) ..	W.
<b>Rhodium</b> .. ..	Rh.	<b>Uranium</b> .. ..	U.
Rubidium .. ..	Rb.	<b>Vanadium</b> .. ..	V.
Ruthenium .. ..	Ru.	Yttrium .. ..	Y.
<b>Selenium</b> .. ..	Se.	<b>Zinc</b> .. ..	Zn.
<b>Silicon</b> (Silicium) ..	Si.	<b>Zirconium</b> .. ..	Zr.

In order to distinguish different kinds of elementary (as well as compound) matter, it is necessary to study carefully the principal physical properties as they present themselves to our senses, such as the state of aggregation, colour, lustre, hardness, density, crystalline structure, the fracture of solid bodies, and lastly, the impression a substance makes upon our sense of taste, odour, and touch. Among the most important of these physical properties are those which can be expressed by figures, such as the specific gravity or density of a body, the temperature at which it passes from one state of aggregation to another, and the crystalline form which it exhibits.

**Summary.**—Elementary as well as compound bodies exist, either in the solid, liquid, or gaseous state. Changes in the mere state of aggregation of bodies are termed **physical changes**.

Mixtures of two or more elementary or compound bodies, unaccompanied by any chemical change, are termed **mechanical mixtures**.

Changes which give rise to a new body or bodies, differing essentially in properties from the original bodies, are called **chemical changes**. The new body or bodies may be formed—1st. By the **combination** of two (or more) simple bodies, perfectly distinct in their properties; or, 2nd. By the **decomposition** of a compound body into two (or more) simpler bodies, differing in properties from the former.

Bodies reacting upon each other are termed **reagents**. The change itself is called a **reaction**.

Bodies which cannot be decomposed by any known process into simpler bodies, differing essentially in properties, are called **simple substances** or **elements**.

Sixty-two elements are known up to the present time.

## CHAPTER IV.

## REDUCTIONS. CHEMICAL AFFINITY.

Oxides are binary compounds. Most oxides hitherto referred to were obtained by a simple process of *addition* of element to element.

A further step towards enlarging our chemical knowledge will naturally be gained by ascertaining whether these binary compounds can be broken up into their component parts or elements; whether, in fact, the *elements contained in oxides can be isolated again*. Chemical processes of this kind are termed *reductions*.

Experiment 8 showed clearly that heat alone can split up an oxide into its two component elements, into mercury and oxygen. Reductions of so simple a nature are, however, rare; and it happens more frequently that the *affinity* which holds elements together in binary compounds is much greater than what we find in the case of the red oxide of mercury, and that heat alone cannot overcome it. In such a case we make use of the stronger affinity which a third element may possess for one of the elements of a binary compound.

Adhesion or cohesion exists between bodies or parts of bodies, and enables them to hold together without altering their properties, and to remain *what they are*. A chemical change, we have learned, produces new bodies, *different in properties* from the original bodies. Hence a chemical compound must form a far more intimate combination, and the union of the elementary component parts must necessarily extend to the smallest possible particles of the body. On this account a distinct name has been given to this uniting force, viz., *chemical affinity*. It may be defined as a *force which draws together the elements of a compound*, firmly linking particle to particle, and *which opposes itself to their separation*.

Chemical affinity varies in degree with the temperature. Lime and carbonic anhydride, *e.g.*, combine readily at the ordinary temperature to form chalk (calcic carbonate), but at a red heat (*e.g.*, in lime kilns) this latter is decomposed again, giving off carbonic anhydride and leaving lime.

Experiment 10 has shown that sodium and potassium possess a greater liking or attraction, or, as we must now call it, a greater *affinity* for oxygen than either magnesium, iron, lead, mercury, or copper. We infer, therefore, that it will be easier to remove the oxygen from mercuric oxide than from soda. This is actually the case, as Experiment 8 proved. If only a slight or weak affinity has to be overcome between the elements composing a binary compound, as in the case of mercuric oxide, heat alone may overcome the force which is opposed to their separation. If, on the other hand, the elements of an oxide are held together by a powerful affinity for each other, inherent in each element—although heat will certainly *help* to overcome the opposition—to overcome it entirely we must

call into action other elements possessing a still stronger affinity for one or other of the component elements of the oxide. Now, to discover the different degrees of affinity which different elements exhibit towards one another, and to be able to select the right element for the purpose of breaking up a binary compound, is a matter of pure experiment. Such knowledge, in fact, constitutes our chemical experience. It is possible to reason from a knowledge of well-established affinities, and frequently to predict by reasoning from analogy, what changes will take place when an element acts upon a binary body. The experience gained by the few simple experiments which have hitherto been described has already taught us that potassium, sodium, and phosphorus possess great affinity for oxygen. Next to these we must classify sulphur, carbon, hydrogen, magnesium, aluminium, zinc, iron, tin, lead, copper, mercury, silver, platinum, gold; and we perceive at once why silver, platinum, and gold are noble metals, namely, because of their extremely slight affinity for oxygen.

**Experiment 31.**—Introduce some cupric oxide or black copper scales (see Experiment 15) into a bulb-tube of hard glass, and pass *dry* hydrogen over it, as shown in Fig. 25. For this purpose the gas may be generated from zinc and

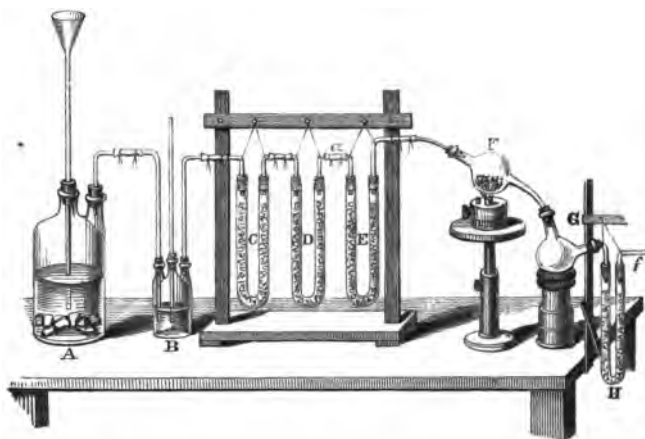


FIG. 25.—REDUCTION OF CUPRIC OXIDE IN A CURRENT OF DRY HYDROGEN.

dilute hydrochloric acid in the Woulfe's bottle A. Commercial zinc is, however, never obtained pure, but contains invariably small quantities of carbon and sometimes of arsenic and sulphur which form gaseous hydrogen compounds possessing a very disagreeable odour. In order to remove these impurities, the hydrogen gas is passed through a Woulfe's bottle, B, containing water—a so-called wash-bottle—and then through several U-tubes, C D E, filled with small pieces of pumice-stone, before it passes over the cupric oxide in F. The pumice-stone in the first U-tube is moistened with a concentrated solution of caustic potash; that in the second with a solution of corrosive sublimate; and that in the third with concentrated sulphuric acid, which retains every trace of moisture which the gas carries with it. The cupric oxide in F is heated by a spirit lamp or gas jet, and is connected with a small two-necked receiver, G, in which the



greater part of the water which is produced by the deoxidation or reduction of the cupric oxide is allowed to condense, and with a U-tube, H, filled with pumice-stone soaked in concentrated sulphuric acid, which absorbs the remaining water.

The bulb-tube is first weighed empty, then with its charge of about 4 grammes (or 60 grains) of previously ignited oxide. The difference in the weight gives the amount of cupric oxide. As soon as the air has been completely displaced from the tube, the gas which issues from the glass jet, *f*, may be lighted and heat applied to the cupric oxide. When the oxide has become sufficiently hot, a change is observed. It begins to glow, the hydrogen flame becomes smaller and smaller, and dies out at last. Moisture condenses in the two-necked receiver, G, and in the U-tube, H, the weight of which has been previously ascertained. If the lamp be removed from time to time the formation of steam ceases, and the hydrogen can be lighted again. By continuing the application of heat, whilst passing a slow current of hydrogen, it is possible to obtain finely-divided metallic copper in the form of a red spongy powder. The experiment is continued till the whole of the oxygen of the cupric oxide has gone to the hydrogen to form water. The bulb-tube is allowed to cool in a current of dry hydrogen. It is then disconnected, the hydrogen displaced by dry air, and the bulb-tube weighed again as speedily as possible. The difference in the weight indicates the loss which the cupric oxide has suffered.

The loss is the same, however often the experiment may be repeated. It is in the proportion of 79.5 to 63.5, or, if we express it in percentage numbers, every 100 parts by weight of cupric oxide lose 20.13 of oxygen.

It is obvious that the water left in the receiver G and the U-tube H must be the result of the oxidation of the hydrogen gas by the oxygen removed from the cupric oxide. The increase in weight, which can readily be determined by a second weighing, consists in fact of the oxygen so removed, and the hydrogen with which it combined to form water; and for every 8 parts by weight of ponderable matter lost by the cupric oxide in the bulb-tube F, we find an increase of 9 parts by weight in the receiver G and U-tube H. We are therefore justified in concluding that oxygen and hydrogen combine in the proportion of 8 to 1 by weight to form water.

This experiment proves clearly that the affinity which hydrogen possesses for oxygen is not sufficient to break up cupric oxide (a binary compound) in the cold, but only when aided by heat. On comparing the change that took place when red mercuric oxide was heated, with the change which took place when hydrogen was passed over cupric oxide, two things become apparent, viz. :—

1st. Both changes are reductions.

2nd. The second reduction is accompanied by an oxidation.

Chemically combined oxygen, as well as free oxygen, or oxygen mixed, with nitrogen as in air, can therefore oxidize hydrogen and convert it into water.

It is of interest, moreover, to observe, how a gaseous body, oxygen, becomes converted into a solid by combining with copper; and on leaving the copper and combining with the gas hydrogen, is converted once more into a gaseous body, steam, which condenses into a liquid body, water.

The oxidation of the hydrogen by means of the oxygen in the cupric oxide, is termed an *indirect* oxidation.

Other metallic oxides can, in like manner, be reduced, and this process of reduction is actually resorted to when pure iron and zinc have to be prepared.

Some oxides, such as magnesia, soda, potash, cannot, however, be reduced in this simple manner. These metals have too strong a hold upon the oxygen; or, in other words, the chemical affinity which they possess for oxygen is greater than that which hydrogen possesses for oxygen, even when aided by strong heat.

From Experiment 1, we have seen that the affinity of the metal sodium for oxygen is sufficiently powerful to decompose water, *i.e.*, to deprive it of its oxygen, and thereby liberate the hydrogen in the gaseous form. The oxidation of the metal sodium was in that case likewise an indirect oxidation.

**Experiment 32.**—Introduce into the bulb of a hard glass tube (Fig. 26) a small piece of sodium, and pass slowly over it dry carbonic anhydride, obtained as shown in Experiment 24. No change takes place. Heat the metal contained in the bulb. It is rapidly converted into the oxide of sodium or soda at the expense of the oxygen of the carbonic anhydride, and carbon separates and remains intimately mixed up with the oxide. Allow to cool and add a little water. The soda dissolves and the carbon floats on the liquid and may be separated by filtration.

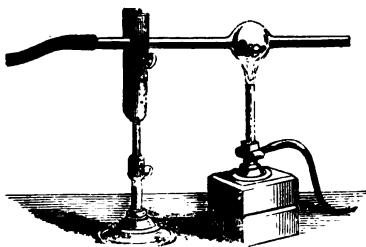


FIG. 26.—REDUCTION OF  $\text{CO}_2$  BY SODIUM.

This experiment, viewed in connection with Experiment 24, proves that carbon can be oxidized directly by passing oxygen over charcoal heated in a tube of *hard* glass; and that the carbonic anhydride so formed can indirectly oxidize sodium, leaving free carbon.

It becomes also apparent that the metal sodium possesses a stronger chemical affinity for oxygen than the non-metal carbon; and yet sodium and potassium are obtained in the metallic state by this very action of carbon upon the oxides of these metals. Here then is an apparent contradiction.

It may be readily explained, however, if we take into account the part which heat plays in these reactions. Carbonic anhydride yields up its oxygen to the metal sodium, when the latter is gently heated, as in the preceding experiment, because *at this temperature* the affinity of the sodium for the oxygen is sufficiently excited to cause the decomposition of the carbonic anhydride. The finely-divided carbon does not, however, react upon the sodic oxide formed, the heat not being sufficient; but if a mixture of soda and carbon be exposed in an appropriate furnace, and in suitable iron vessels, to a strong heat, the affinity of the carbon for oxygen becomes stimulated to a sufficient degree to deprive the sodic oxide of its oxygen. The gaseous product of the indirect oxidation of the carbon escapes, together with the vapour of the metal sodium.

The latter can be condensed into a solid body, whilst the carbonic oxide can no longer exert any action upon the metal at a low temperature.

Such chemical changes depend upon *reciprocal affinities*.

Phosphorus, we have seen, possesses, like sodium or potassium, a strong affinity for oxygen. But by mixing its oxide, phosphoric acid, or substances containing phosphoric acid, such as ground bones with charcoal, and exposing the mixture in an iron retort to a strong furnace heat, phosphorus distils off, and can be condensed in water, whilst the oxides of carbon escape as gases. It is evident then that the easy volatilisation of sodium and phosphorus facilitates the process of reduction; whereas metals, such as magnesium and aluminium, which possess less affinity for oxygen, but volatilise with more difficulty than sodium or phosphorus, cannot be reduced from their oxides by the action of carbon.

**Summary.**—*Oxides are binary compounds, formed by the direct or indirect combination of oxygen with another element. The operation by which a compound body is resolved into its elements is called a reduction (resolution).*

*The force which draws together bodies of the same or of a different chemical nature, and which opposes itself to their separation, is called chemical affinity.*

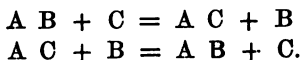
*The intensity of a chemical reaction depends upon the strength of the chemical affinity which exists between different kinds of elementary matter.*

*Elements which possess the greatest affinity for oxygen constitute the most powerful reducing agents.*

*A reduction is frequently effected by the displacement (substitution) of one element in a binary body by another element.*

*Such displacement depends not only upon the degree of affinity, but also upon the temperature, state of division, &c., of the bodies reacting upon each other.*

*Reactions are termed reciprocal, when the result of one reaction constitutes the basis or starting-point of another, e.g.,*



## CHAPTER V.

**REDUCTION BY MEANS OF ELECTRICITY**  
(Electrolysis). **OZONE.**

THE reductions hitherto studied have been of a twofold nature :

- 1st. A simple decomposition of an oxide by heat into its component parts or elements.
- 2nd. A decomposition by the aid of an oxidizable body, either without heat or assisted by heat.

Electricity furnishes us with additional means of splitting up many chemical compounds into their elementary component parts. Voltaic electricity\* is almost exclusively used for this purpose.

On plunging the electrodes of a voltaic battery (consisting of two zinc-carbon cells at least) into water to which a few drops of sulphuric acid have been added, decomposition of the water takes place. Oxygen escapes from the positive electrode connected with the carbon end, and hydrogen from the negative electrode connected with the zinc end of the battery. If the end of the wire of the positive electrode consists of a readily oxidizable metal, such as iron or copper, no oxygen is evolved, as the gas combines with the metal the moment it leaves the hydrogen of the water, and forms with it an oxide. Hydrogen, on the other hand, is evolved at the negative pole in the free state. In order to obtain oxygen likewise in the free state, platinum electrodes are employed, and both gases can thus be collected either separately or mixed together in the same vessel.

**Experiment 33.**—On introducing the platinum electrodes into water, the conductive power of which has been increased by the addition of a few drops of sulphuric acid, we observe immediately small gas bubbles forming on the strips of platinum, and escaping through the liquid (Fig. 27).



FIG. 27.

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\* The student should study in some good manual of Natural Philosophy the laws of the electric current, and make himself familiar with the apparatus employed for producing voltaic electricity.

**Experiment 34.**—A small bottle (Fig. 28) is fitted with a cork and a short glass tube, bent at a right angle. Two platinum wires pass likewise through the



FIG. 28.

cork, and end in small strips of platinum. The bottle is nearly filled with acidulated water, and the platinum electrodes are connected by means of copper wire with the voltaic battery. Gas bubbles are instantaneously seen to form on the platinum strips, and to detach themselves gradually; they rise through the liquid, and escape through the delivery-tube into the cylinder, C, placed full of water over the pneumatic trough. The gas so collected detonates with great violence when a light is applied to it.

It constitutes, in fact, an explosive mixture of two volumes of hydrogen, and one volume of oxygen.

**Experiment 35.**—These volume proportions are shown by introducing the platinum electrodes, resting on a piece of gutta-percha, into separate cylinders of equal diameter, as shown in Fig. 29. The gas arising from the negative

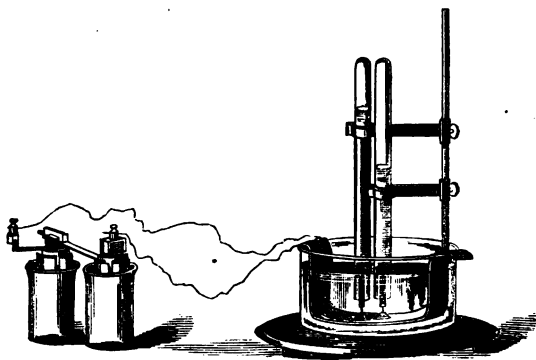


FIG. 29.

electrode occupies twice the space from that given off at the positive electrode. On examining the gases in the usual way, by applying a light, the larger volume of gas burns with the characteristic flame of hydrogen; the smaller volume does not burn, but supports combustion; it is oxygen gas.

**Experiment 36.**—In order to show that the gases evolved at the positive and negative electrode always come off in the proportion of one volume of oxygen to two volumes of hydrogen, an apparatus proposed by Dr. Hofmann (Fig. 30) may be used with great advantage. It consists of a U-tube, connected from its bend with an equally wide long upright tube. The two tubes of the U-tube end in two narrow tubes, provided with glass stopcocks. The apparatus is filled with acidulated water, so that the U-tube is quite full up to the stopcocks. The

main tube must be long enough to receive the liquid contained in both limbs of the U-tube. The two electrodes are introduced from below into the U-tube. On completing the circuit oxygen is seen to be evolved at the positive and hydrogen at the negative pole; the quantity of the latter is, moreover, seen to be always just double that of the former gas, however much or however little water we may decompose by the voltaic current. The gases collected in the limbs of the U-tubes are tested by opening the stopcocks, applying successively a glowing chip of wood or a lighted taper to the gas which issues from the narrow tube.

Our attention is at once fixed in the two last experiments by the *constant volume proportions* in which the two gases are obtained on electrolysing water. In fact, as often as the experiment is repeated, one volume of oxygen and two volumes of hydrogen are invariably obtained. We have, then, a right to infer that the two gases are really combined in water in these proportions.

**Experiment 37.**—It remains now only to prove that two volumes of hydrogen and one volume of oxygen, when mixed and exploded in a eudiometer-tube,\* *a* (Fig. 31), combine in the very same proportions to form water. We employ for this purpose a narrow glass tube, *a*, accurately graduated for holding the explosive mixture, and place the tube in mercury contained in the glass cylinder, *c*. The electric spark is made to pass between two platinum wires, fused into the upper part of the tube at *b* and *c*, which nearly touch each other within the tube, and end outside in two small loops, one of which, *b*, is connected by means of a small chain with the outer coating of a Leyden jar, charged with electricity: and by touching the other loop, *c*, with the knob of the jar, a spark passes through both platinum wires, and fires the gaseous mixture.

The heat which is produced by the chemical combination of the hydrogen and oxygen, momentarily expands the steam, the product of the chemical combination, considerably. The eudiometer should, therefore, never be more than half full of gas, and should, moreover, be pressed down firmly upon an india-rubber pad at the bottom of the mercury. As soon as it has sufficiently cooled, the steam condenses on the sides of the eudiometer, and the mercury rushes in and fills nearly the whole of the space occupied previously by the two gases.

If the mixture be diluted with a large excess of either hydrogen

\* So called from *εὐδία*, calm air, and *μέτρον*, a measure.



FIG. 30.

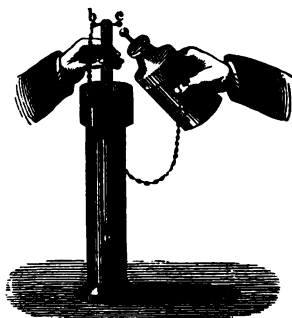
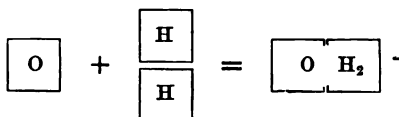


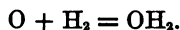
FIG. 31.

or oxygen, the explosion becomes less violent, and less heat is given out. The hydrogen gas may in this manner be burnt almost without explosion, and if the dilution be carried sufficiently far, the gases combine only locally when a light is applied, and the combustion does not spread to the surrounding gaseous mixture. The excess of oxygen or hydrogen is found in the eudiometer-tube unacted upon after firing the mixture. One volume of oxygen unites exactly with two volumes of hydrogen, no matter in what proportions these gases may have been previously mixed. By rarefying the gaseous mixture before exploding it by means of the electric spark, the violence of the explosion is likewise considerably reduced.

This leads us to consider the combining relations between elementary bodies, of which, in the processes of oxidation and reduction hitherto studied, no account was taken, viz., *the quantitative proportions in which elements combine*. The combination of water by volume may be represented by the following scheme:—



The small squares are made to represent the volume units of the elementary gases; and to represent water symbolically we should write  $\text{O}\frac{\text{H}}{\text{H}}$ , or  $\text{OH}_2$ , the formation of water by the combination of oxygen and hydrogen being expressed symbolically by the equation—



Now if two elements such as oxygen and hydrogen are found to combine invariably *in fixed volumes*, it is clear that these two gases must also combine *in fixed proportions by weight*, for each of these gases has its own weight or specific gravity. Hydrogen has a specific gravity of 0.0691, and oxygen of 1.1056, when compared with air; hydrogen is therefore 16 times lighter than oxygen, thus:—

$$\frac{1.1056}{0.0691} = 16.$$

If 1 litre of hydrogen gas weighs 1, a litre of oxygen must weigh 16, and since always two parts *by volume* (2 litres) of hydrogen are required to combine with one part *by volume* (1 litre) of oxygen, two parts *by weight* of hydrogen will be necessary to combine with 16 parts *by weight* of oxygen, and in order to express symbolically the combination by volume and by weight by one and the same scheme or formula, water is written  $\text{O}\frac{\text{H}}{\text{H}}$ , or  $\text{OH}_2$ , in which formula each H not only expresses hydrogen, but one part by weight

and one part by volume, and the O not merely oxygen, the element, but 16 parts by weight and one part by volume of oxygen.

Water is then composed as follows:—

By volume.	By weight,
2 vols. of H	2 parts by weight of hydrogen.
1 vol. of O	16 parts by weight of oxygen.

Or in 18 parts by weight of water (say 18lb.) there are—

2lb. of H, and  
16lb. of O;

and as this composition of water is constant, we can readily calculate from these figures how much hydrogen or oxygen is contained in any given quantity of water.

In order to know, *e.g.*, how much hydrogen is contained in 100lb. of water, we have the proportion—

$$18 : 2 :: 100 : x$$

$$x = 11.11 \text{ lb. of hydrogen.}$$

The percentage composition (by weight) of water is therefore—

Hydrogen	11.11
Oxygen	88.89
	<hr/>
	100.00

Now, in Experiment 31 we likewise obtained water, as the product of the reduction of cupric oxide in a current of dry hydrogen gas, and we found that the oxygen and hydrogen combined in the proportion of 8 to 1.

It is obvious, however, that the water so obtained had the same composition as the water decomposed by electrolysis in Experiment 36, and we have, therefore, no hesitation in altering the above figures to the proportion of 16 of oxygen to 2 of hydrogen, *so as to represent by the same formula, volume combination as well as combination by weight.*

**Ozone.**—It will probably not have escaped notice that a peculiar odour was produced when water was decomposed by voltaic electricity in Experiment 33. A similar odour may be noticed whenever an ordinary frictional electrical machine is set in motion, an odour which strongly resembles the sulphurous smell perceived in the air after some vivid lightning. A special apparatus constructed for electrifying air produces a like odour. Schoenbein first noticed the similarity between the odour produced by chemical discharges, and that which accompanies the electrolysis of water, or when phosphorus is slowly oxidized.

**Experiment 38.**—Cleanse a few short sticks of phosphorus under water from any adhering white oxide, and place them at the bottom of a perfectly clean large flask (Fig. 32) with enough water to cover about half of the phosphorus. Loosely cover the flask with a glass plate, and let it stand quietly for half an hour at the ordinary temperature, then invert it over water and allow the phosphorus to fall out. Replace the glass plate and remove the flask from the



water. Introduce now a broad strip of freshly-prepared, moist iodized starch paper.\* The paper immediately turns blue owing to the liberation of iodine, which forms with the starch a blue compound. Ordinary air or oxygen is without action upon iodized starch-paper, showing clearly that the air has been chemically acted upon by the phosphorus. The paper remains unchanged if the phosphorus be left too long in the flask.



FIG. 32.—PREPARATION OF OZONE.

Several other methods for the preparation of ozone will be referred to hereafter.

It has been found that only the oxygen of the air and not the nitrogen is chemically altered by the action of the phosphorus; that its properties become, so to speak, intensified. Hence ozone has also been called active oxygen. On account of its odour it has received the name ozone from ὄζω, I smell. Ozone differs from oxygen by being denser,—it is half as heavy again, three volumes

of oxygen furnishing by condensation two volumes of ozone. It has, however, never been obtained free from admixture with a very large proportion of air or oxygen. Ozone is not soluble in water. Oil of turpentine absorbs the ozone only from a mixture of ozone and oxygen, leaving the oxygen untouched. The density of ozone has been determined by observing the diminution in the volume of the mixture of the two gases.

When ozonified air is inhaled it produces a feeling of irritation in the lungs. When heated to  $290^{\circ}\text{C}$ ., or when passed over black manganic oxide or similarly constituted bodies, ozone is changed into ordinary oxygen, without these oxides undergoing any permanent change. It exerts a powerfully oxidizing action upon substances which are not acted upon by ordinary oxygen. It immediately oxidizes the common metals as well as dry mercury, and even silver when moist. It has a powerful bleaching action, and destroys effluvia far more effectually than any other deodorising agent known. Traces of ozone are usually present in country air, especially after a thunderstorm, but more so in sea air when the wind blows off the sea, rarely, however, in the atmosphere of crowded towns; in damp and foggy weather less ozone or none at all is found in the air. Most plants whose growing is favoured by bright sunlight give it out, mixed with oxygen, although in exceedingly small quantities.

**Summary.**—*Voltaic electricity constitutes a powerful reducing (resolving) agent.*

\* Prepared by soaking unsized paper, *e.g.*, some strips of Swedish filtering paper, in a cold dilute solution of starch (1 part of starch dissolved in 10 of boiling water) and potassic iodide (KI) ( $\frac{1}{10}$ th of a grm.), and drying by suspending the moist strips of paper over some white cotton yarn. Keep the dried papers in the dark in a well-stoppered bottle till required for use.

*Gaseous elements combine in very simple definite proportions by volume and by weight. These proportions are constant.*

*Symbolic representation of chemical changes expresses by one and the same formula both volume combination and combination by weight.*

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## CHAPTER VI.

### CONSTANT COMBINING PROPORTIONS, ATOMS AND MOLECULES, ATOMIC, AND MOLECULAR WEIGHT. CHEMICAL FORMULÆ. SYMBOLIC EQUATIONS.

WE have just established experimentally that the combination by volume of hydrogen and oxygen remains invariably the same, whether large or small volumes of the two gases enter into chemical combination, that the combining ratio of two volumes of hydrogen to one volume of oxygen gas remains in fact *constant*, and that the combining proportion by weight must, for the same reason, be likewise constant, viz., as 2 to 16.

We can conceive, moreover, that chemical combination does take place between minutely small proportions by volume of the gaseous bodies hydrogen and oxygen—between quantities far beyond the reach of experiment—and yet be convinced that all such combinations, even between the smallest imaginary gaseous particles of these elementary bodies, must take place in a like ratio of two volumes of the one to one volume of the other, and that the water so formed must possess properties perfectly identical with those observed in the water resulting from the combination of large volumes of hydrogen and oxygen. It can be proved experimentally also that when a mixture, containing an excess of either element, is exploded in a eudiometer, chemical combination takes place only so far as to satisfy the requirements of this law of definite proportions, viz., between two volumes of hydrogen and one volume of oxygen; and the portion of the element that happens to be in excess of this ratio, will remain in a free or an uncombined state mixed with the aqueous vapour. *The combining proportions remain constant.*

The composition of water by weight and by volume is capable of being demonstrated by the two methods usually pursued in chemical investigations: viz., by the *analytical*\* method, for we can break up water (comp. Experiment 36) into its constituent parts; and by the *synthetical*† method, for we are able to obtain water by the direct union of the two gases hydrogen and oxygen in the eudiometer tube. We have learnt to destroy water and build it up again. The means at our disposal for proving the chemical composition of water

\* From ἀνάλυσις, a loosening.

† From σύνθεσις, a putting together.

are in fact more ample than those we possess for demonstrating the constitution of most other bodies. We can break up bodies readily enough into their constituent elements, but are sometimes unable to build them up again.

If water, then, results from the chemical combination of smallest particles of two kinds of gaseous elementary matter in immutably constant proportions, it may legitimately be conceived, that chemical combination *always* takes place between such smallest particles of matter, and that every process of chemical combination between large or small bulks or volumes of gaseous matter is, in fact, merely a repetition of a process of combination between smallest possible gaseous particles or volumes; also, that chemical bodies generally consist of a number of smallest particles of matter, capable of entering into combination with smallest particles of other kinds of elementary matter.

We have no conception *what* these smallest particles are, nor do we know what is their size, shape, etc. Matter itself being as yet unknown to us, need we wonder that the very existence, size, shape, etc., of the smallest particles of matter should not be capable of experimental demonstration? Where experiment fails to throw light upon the absolute nature of the constant chemical combining proportions, and can at best only supply us with relative data, hypothesis steps in.

*Dalton* assigned to the smallest particles of matter, between which chemical action takes place, finite proportions, and called them *atoms*;\* assuming them to consist of the smallest particles of elementary matter which are capable of existing in *chemical combination*. According to this theory, known as the *atomic theory*, all elementary matter consists of atoms which, on entering into combination with other atoms of similar or dissimilar elementary matter, form molecules, *i.e.*, little masses, from *moles*, a mass. A *molecule* of matter is the smallest quantity of a substance—elementary or compound—which is capable of existing *in the free state*.

The weight of hydrogen which combines with or is expelled from other gaseous, liquid or solid elementary matter, being relatively smaller than that of any other elementary body known to us, has, on this account, been adopted by chemists as a convenient unit or standard for determining the relative combining weights of elementary bodies. The smallest proportion by weight in which an element enters into or is expelled from a chemical compound—the smallest weight of hydrogen so entering or leaving a chemical compound being chosen as unity—constitutes the relative combining weight of such element. The observation† that the weight of an element in the form of gas or vapour, under like conditions of temperature and atmospheric pressure, occupies the same volume as one part by weight of hydrogen, corroborated the relative combin-

\* From *ἄτομος*, indivisible.

† Other considerations have guided chemists in the determination of atomic weights upon which we cannot, however, touch, as we lack as yet the necessary experimental data.

ing weight. These proportional numbers are called *atomic weights*. They are purely arbitrary numbers. The atom weight of any other element might have been chosen as the standard—in fact, oxygen at one time constituted the standard and had the combining weight 100 assigned to it—without in the least disturbing the law of constant combining proportions. By making the atomic weights of other elements the standard of comparison, as many series of atomic weights might be obtained as there are elements; and yet all would satisfy the requirements of the atomic theory, since they would all express correctly the **relative combining weights of elementary bodies**.

In water, we have already seen, there are two parts by weight of hydrogen—or as we must now call it, two atom weights—combined with 16 parts by weight or one atom weight of oxygen, the gaseous atom oxygen weighing, as we have seen, 16 times heavier than an atom of hydrogen. In like manner we have found by experiment that the metal mercury combines with oxygen in the proportion of 200 to 16, and we have no hesitation to assign to the metal mercury the atomic weight 200: that is to say, one atom of mercury, weighing 200, by combining with one atom of oxygen, to form 216 parts by weight of mercuric oxide, takes the place of two atoms of hydrogen in water. Copper, we have seen, combines with oxygen (compare Experiment 31). The increase in weight was invariably as 63·5 of copper to 79·5 of the oxide. The atomic weight of copper must therefore be 63·5; i.e., one atom of the element copper, weighing 63·5, entered into combination with 16 parts by weight of oxygen and replaced two atoms of hydrogen in water.

It is obvious that we should have no difficulty in fixing the atom weight of copper if this elementary body could be obtained like hydrogen in the gaseous condition. We should simply have to determine the specific gravity of a given volume, say one litre of gaseous copper, and divide the weight of such volume by the weight of an equal volume of hydrogen. We should next have to double the number so obtained, because the atom copper takes the place of no less than two atoms of hydrogen. We can conceive, however, that the oxygen gas which existed in a solid condition in combination with the metal copper, and which was removed in Experiment 31 by the action of the gaseous hydrogen in the form of water, leaving behind solid metallic copper, was attacked by one hydrogen atom after another, and that for every two atoms of hydrogen, with which an atom of oxygen combined, one atom or 63·5 parts by weight of copper were set free, so as to leave for every 79·5 parts by weight of cupric oxide which were acted upon, 63·5 parts by weight of metallic copper, and 18 parts by weight of water. If, then, combination between smallest particles by weight of oxygen and hydrogen can be conceived, it is equally conceivable that smallest particles (or atoms) of the solid body copper were combined with smallest particles (or atoms) of oxygen, and that the binary compound cupric oxide consisted likewise of smallest particles (or atoms) of copper and oxygen, combined in immutably constant proportions by weight.

Now, in anticipation of experimental confirmation, we may say that the same holds good for other elements. The atomic weights were found to differ for every element, and had to be determined in every single case by experiment. Such quantitative experiments are among the most difficult and delicate chemical operations; let it suffice, then, to remark that the law of combination according to constant proportions by weight and by volume, has been established experimentally with the utmost precision, and that we shall have frequent opportunity, as we enlarge our knowledge of chemical compounds, to satisfy ourselves of its perfect consistency.

The symbols which have hitherto merely represented the individual elements gain thus in interest, since they not only recall the *name* of the element, but indicate at the same time *one atom* of such element, together with its particular *combining weight* and, with few exceptions, its *combining volume*.

The following tables give the names, symbols, and atomic weights of the 36 most important elements:—

#### NON-METALLIC ELEMENTS (*Metalloids*).

Oxygen .....	O	16	Nitrogen .....	N	14
Sulphur .....	S	32	Phosphorus .....	P	31
Chlorine .....	Cl	35.5	Carbon .....	C	12
Bromine .....	Br	80	Boron .....	B	11
Iodine .....	I	127	Silicon .....	Si	28.5
Fluorine .....	F	19	Hydrogen .....	H	1

#### METALLIC ELEMENTS.

Light Metals:			Heavy* Metals:		
Potassium .....	K	39	Chromium .....	Cr	52.5
Sodium .....	Na	23	Iron .....	Fe	56
Magnesium .....	Mg	24	Zinc .....	Zn	65
Barium .....	Ba	137	Manganese .....	Mn	55
Strontium .....	Sr	87.5	Cobalt .....	Co	58.8
Calcium .....	Ca	40	Nickel .....	Ni	58.8
Aluminium .....	Al	27.5	Tin .....	Sn	118
			Gold .....	Au	196.7
			Platinum .....	Pt	197.4
			Lead .....	Pb	207
			Mercury .....	Hg	200
			Silver .....	Ag	108
			Copper .....	Cu	63.5
			Cadmium .....	Cd	112
			Bismuth .....	Bi	208
			Arsenic .....	As	75
			Antimony .....	Sb	122

\* The metals which possess a higher specific gravity than 5, and which are not acted upon at the ordinary temperature, by the oxygen of the air, are called heavy metals.

Combination by volume, we have seen, takes place in accordance with the law of constant combining proportions by weight; *i.e.*, two volumes of hydrogen will invariably combine with one volume of oxygen to form water (steam).

What volume, however, does the steam so formed occupy? This question can only be answered experimentally.

In order to measure the volume of steam left in the eudiometer-tube (Experiment 37), hydrogen and oxygen gases must be exploded at a temperature at which the steam produced cannot condense. Dr. Hofmann has devised an apparatus\* which accomplishes this in a very elegant manner.

**Experiment 39.**—A mixture of two volumes of hydrogen and one volume of oxygen is introduced into a U-tube A (Fig. 33), the eudiometer-tube is, how-

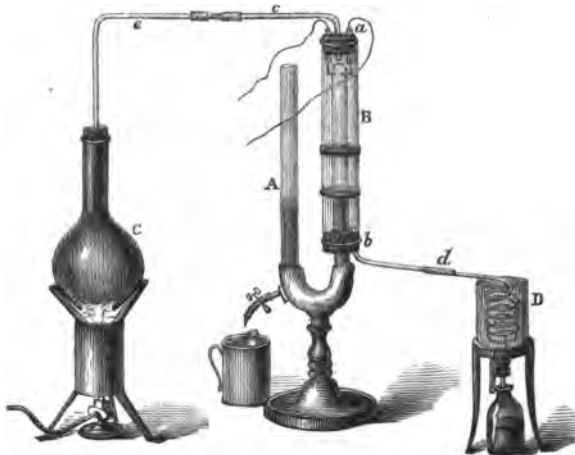
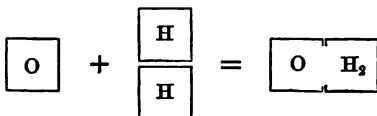


FIG. 33.—VOLUMETRICAL COMPOSITION OF STEAM (HOFMANN).

ever, surrounded by a jacket consisting of a wider glass tube, B, fixed over it airtight by means of corks. The vapour of amylic alcohol, a liquid boiling at  $132^{\circ}\text{C}$ ., is made to pass from the flask C through the intervening space, and out at *b*, *d*, to be condensed in the worm D. The gaseous mixture acquires thus rapidly a temperature of  $132^{\circ}\text{C}$ . It is then exploded in the usual manner. The two gases combine and form water, which remains, however, as steam, and is found when the pressure in the two limbs of the apparatus is equalized, to occupy only two-thirds of the volume which the mixture of hydrogen and oxygen occupied before explosion.

Consequently three volumes of gas contract into two volumes.



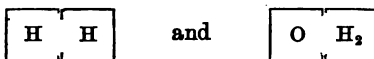
\* Modern Chemistry, page 53.

A molecule of steam occupying two volumes is, therefore, made up of two volumes of hydrogen and one volume of oxygen, and the weight of one volume of steam must be the weight of one volume of hydrogen and half a volume of oxygen, or  $1 + 8 = 9$ . The specific gravity of steam is therefore 9; *i.e.*, one litre of steam is nine times as heavy as one litre of hydrogen gas—the unit of comparison adopted for gas volumes—and its actual weight will be found by multiplying the weight\* of a litre of hydrogen .0896 grm. by 9:

$$.0896 \times 9 = .8064 \text{ grm.}$$

A similar contraction of volume frequently takes place, when other gaseous mixtures combine chemically; the resulting gaseous volumes are (with a few exceptions) two-volume vapours.

Compound bodies can have no atom volume, they possess only molecular volumes. Hence if we wish to compare gaseous elements and compounds with each other, we have to adopt molecular weights, both for elements and compounds, as the measure of the combining quantities. Thus, in order to compare the volume of the element hydrogen with the gaseous compound body, steam, we have to compare the molecular volume of hydrogen with the molecular volume of steam—



Other reasons, also, to which we cannot refer here, render it desirable that hydrogen, when regarded in relation to other gaseous bodies, should be expressed as the molecule H H, or H<sub>2</sub>, and not as H, the atom. The same applies to other gaseous elements. Since the volume of a gas varies with the pressure of the atmosphere and the temperature, these molecular gas volumes would necessarily be of variable dimensions, a conception which runs counter to the idea we have formed of the constitution of atoms and molecules. All gases expand, however, under the influence of heat in the same ratio. For every degree of the centigrade thermometer scale above 0° C., they expand .3665 per cent., or, less accurately,  $\frac{1}{273}$  part of their bulk at 0°. The average weight of the atmosphere at the level of the sea is that of a column of mercury 760 millimetres† high. Now, according to the law of Boyle and Marriotte, the volume of a gas is inversely, and its density directly, as the pressure which it sustains if the temperature remains constant. We have, therefore, no difficulty in reducing gases to the standard agreed upon by chemists, *viz.*, a temperature of 0° C. and 760 mm. atmospheric pressure, at whatever temperature or barometrical pressure they may have been measured.

\* Dr. Hofmann assigned the name *crith* (from *κριθ*, a barleycorn) to the weight of 1 litre of hydrogen, .0896 grm. at 0° C., and 760 mm. barometrical pressure.

† The student should make himself familiar with French weights and measures. (See Tables in Appendix.)

**EXAMPLE.**—A gas volume, say 100 cubic centimetres, was measured when the temperature of the gas was 15° C., and the atmospheric pressure 770 mm. What volume will the gas occupy at 0° C. and 760 mm. pressure?

Correction for temperature—

1 cc. at 0° expands into  $1 + (15 \times .003665)$  at 15° C.  
 $1.054975 : 1 :: 100 : x \quad x = 94.7889$  cc.

Correction for pressure—

$760 : 770 :: 94.7889 : x$ . Ans. = 96.0360 cc.

**Multiple Proportions.**—If the conception which we have acquired of atoms be correct, it follows of necessity that only *whole* or undivided atoms can combine with each other. There is no reason, however, why *several* atoms of one element should not be capable of entering into combination with one or several atoms of another element to form a new compound. Such compounds can be represented symbolically by writing the symbols of the component elements side by side, indicating the number of atoms by placing a small figure after the symbol to be multiplied. When two or more elements combine in single or multiple proportions, the symbolic expression of such combination constitutes a *chemical formula*. A figure placed on the left of the formula or group of elements multiplies every following element, or the sum of all the component parts of the chemical formula. The sign + is employed to indicate the addition to, the sign — the removal or subtraction of one elementary or compound body from, another elementary or compound body.

The sign = should be interpreted by *furnishes*, rather than by the arithmetical meaning *equal to*. Thus 2 atoms of hydrogen, plus 1 atom of oxygen, furnishing water, are expressed symbolically by the equation  $H_2 + O = OH_2$ .

With the experimental data which are at present at our command, we must content ourselves with merely stating that sulphur and oxygen combine in the proportion of one atom of sulphur to two atoms of oxygen to form sulphurous anhydride,  $SO_2$  (Experiment 22). The change is expressed by the chemical equation:— $S + O_2 = SO_2$ . Two atoms of phosphorus unite with five atoms of oxygen to form phosphoric anhydride,  $P_2O_5$  (Experiment 23), equation:— $P_2 + O_5 = P_2O_5$ ; carbon with two atoms of oxygen to form carbonic anhydride,  $CO_2$  (Experiment 24), equation:— $C + O_2 = CO_2$ , and we shall hereafter have to consider many more instances of combination in multiple proportions of a similar nature. We shall also shortly learn that sulphur can combine with three atoms of oxygen, and carbon with one atom as well as with two, that in fact several combinations are possible between two elements, without prejudice to the law of constant combining proportions by weight.

There exist scarcely any chemical elements between which at least two combinations could not take place, whilst there are many elements which can combine with others in three, four, five, and more proportions. As the number of atoms accumulates in a com-



pound, its molecular structure becomes more and more complex, but the combining proportions by weight and by volume stand in a simple ratio to one another, and will be invariably multiples of the simpler combining proportions.

**Summary.—Law of Constant Combining Proportions.**—*All elements combine according to constant proportions by weight. The numbers which express the respective weights of the elements so combining are proportional numbers. The unit of comparison accepted by chemists is the weight of hydrogen, on account of its being less than that of any other element.*

*The smallest proportion by weight in which an element enters into or is expelled from a chemical compound constitutes its atomic weight, the weight of hydrogen being taken as unity.*

*An atom is the smallest particle of matter capable of entering into, or existing in a state of chemical combination.*

*A molecule is the smallest particle of matter capable of existing in the free state.*

*A molecule consists, except in a few cases, of at least two atoms. The atoms of each kind of isolated elementary matter exist, with few exceptions, in combination with each other or are associated in pairs, and constitute then an elementary molecule.*

*The molecular weight of a compound is, with few exceptions, identical with its atomic weight.*

*The molecular volume of a compound equals, with very few exceptions, the molecular volume of hydrogen at the same temperature and pressure.*

*Hence the law:—Equal volumes of all gases and vapours contain at the same temperature and pressure an equal number of molecules, and the molecules of all compounds in the gaseous or vaporous condition, no matter how great may be the aggregate volume of their constituents, occupy, with very few exceptions, one uniform volume, when compared at the same temperature and pressure, viz., that of two volumes, or one molecule of hydrogen.*

**Law of Multiple Proportions.**—*When two elements combine with each other in more than one proportion, the quantities by weight of the one element, which combine with a constant quantity of the other, are invariably integer multiples of its smallest combining quantity.*

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## CHAPTER VII.

**WATER. METALLIC AND NON-METALLIC OXIDES.  
ACIDS. ALKALIES. SALTS. BASIC OXIDES.**

WATER plays a most important part in nature. Its great importance was recognised long before its chemical composition was understood, for it was one of the four elements of which, before the dawn of modern chemistry, matter was supposed to consist. Water covers the greater part of our globe; it forms part of most mineral, vegetable, and animal bodies, and is, like air, absolutely necessary to vegetable and animal growth.

Small quantities of pure water may be prepared synthetically by the direct combination of hydrogen and oxygen (comp. also Experiments 6, 28, 37, 39).

**Experiment 40.**—Introduce a jet of burning hydrogen into a bell-jar supplied with oxygen in the manner shown in Fig. 34. Both gases should be carefully dried, and the glass jar kept cool by means of a damp cloth. In a short time the inside of the jar becomes overcast with watery-vapour which condenses and runs down in drops, the water accumulating in the lower vessel. In this manner a quantity of water may be procured sufficient to study its properties.

Larger quantities of pure water are usually obtained by a process of *distillation*,\* i.e., by condensing steam by means of a Liebig's glass con-



FIG 34.—COMBUSTION OF HYDROGEN IN OXYGEN.

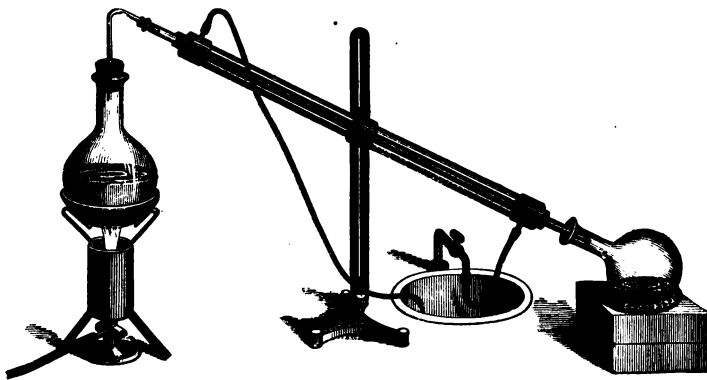


FIG. 35.—DISTILLATION OF WATER.

\* This chemical operation effects the separation of a *volatile* from a less

denser (Fig. 35), or a tin worm (lead is perceptibly dissolved by pure water). *Distilled* water thus obtained is a limpid colourless liquid, without odour or taste. It has no action upon test papers, and can be volatilised without leaving any residue. Water evaporates at all temperatures, and passes off into the air as an invisible vapour (steam). The evaporation is more or less active all over the surface of our globe, so that the atmosphere is everywhere charged with aqueous vapour. The quantity of moisture in the air varies, however, according to the natural conditions which favour or retard the evaporation of the water. The vapour of water being lighter than air (the sp. gr. of steam is only .622 as compared with air), rises till it reaches the upper and colder regions of the atmosphere, where it is condensed into masses of clouds which float on the air, till they become too heavy to be supported any longer, when the water is returned to the earth in the form of dew, mist, rain, snow, hail, etc., etc. A natural process of *distillation* is thus constantly going on all over the globe, and rain water stands in point of purity next to distilled water. It contains, however, the gases of which our atmosphere is composed, dissolved in it, usually to the extent of 3 to 5 per cent. of its own bulk, besides traces of ammoniac nitrate and nitrite, and particles of solid suspended matter washed out of the air.

The presence of air in rain water is necessary for aquatic vegetable, and animal life. Rain water exerts a certain solvent action on the surface matter of our earth, varying in degree according to the nature of the soluble matter with which it comes in contact. Granite, sandstone, slate, and other hard rocks are but little acted upon. Rain water falling upon mountainous formations mainly composed of these rocks, runs off the surface almost pure, generally holding in solution only a little organic and mineral or saline matter. Such waters we meet with for instance in the Welsh and Cumberland lakes, and in Loch Katrine, from which Glasgow draws its water supply.

The waters of lakes and rivers contain, as a rule, less mineral matter in solution than spring waters. Rain sinks into the earth through porous mineral strata of various composition, upon all of which it exerts more or less solvent action, and when the collected waters issue again in natural or artificial springs, they are charged with varying quantities of mineral (saline) substances.

Waters coming from the chalk formation contain chiefly chalk or calcic carbonate, as well as magnesian carbonate in solution. These mineral bodies are held in solution by gaseous carbonic anhydride. Strata of gypsum yield gypsum or calcic sulphate to the water; others are acted upon in an analogous manner.

The amount of solid matter which different spring waters hold in solution varies considerably. A water is considered no longer

volatile or *fixed* body (in the case of natural waters from the mineral or saline constituents which are left behind). The distilling apparatus, flask, retort, etc., must be provided with a *condenser* only, if the substance becomes vaporized at a low temperature. The product of the distillation is called *distillate*, and is usually received in a flask or other vessel, called a *receiver*.

wholesome if it contain more than 1 grm. of mineral matter per litre (= 70 grains per gallon) in solution. Good potable waters should never contain more than a few grains of saline matter per gallon, and should be all but free from readily decomposable organic matter. River and spring waters often contain large quantities of organic matter, if the water which they receive runs over manured and well-cultivated land, or if, from gross ignorance and culpable neglect, sewage is allowed to flow into them. Nature has happily provided running streams with the power of destroying soluble organic matter—a power which is due to the oxygen of the air dissolved in the water. The organic matter is rapidly oxidized, and is converted into harmless products of oxidation, viz., water, carbonic, nitrous, and nitric acids (nitrites and nitrates).

When natural waters are charged with still larger quantities of mineral substances, such as common salt or sodic chloride, sodic sulphate (Glauber's salt—*e.g.*, Cheltenham waters), magnesian chloride or sulphate (Epsom salts), calcic chloride and others, they are termed *mineral* waters. Waters which hold iron salts in solution (carbonate or chloride) are called *chalybeate* waters. They have an inky taste, and on exposure to the air deposit iron rust. Others are called *mineral* waters, because they hold large quantities of gaseous matters in solution, such as the well-known *acidulous* Seltzer water, which is strongly charged with carbonic anhydride, a gas which causes the water to effervesce strongly. *Sulphurous* or *hepatic* waters, such as the water of Harrogate, exhibit a strong odour of rotten eggs (sulphuretted hydrogen).

Inland lakes which have no outlet are usually found charged with very large quantities of saline matter. The water of the Dead Sea contains as much as 12,600 grains, and that of the Great Salt Lake 22,000 grains per gallon. Some springs such as the so-called Geysers of Iceland and California, issue boiling hot from the earth, and deposit silica on cooling. The density of all such waters is considerably greater than that of pure water.

The chemical composition of water has already been established both synthetically and analytically. It is a binary compound, an oxide of hydrogen. Other elementary bodies, we have seen, combine likewise with oxygen to form oxides—bodies which differ, however, very much from each other in their properties. The metals sodium or potassium when burning in dry oxygen form the binary compounds potassa or oxide of potassium, and soda or oxide of sodium. Both these oxides, together with the oxides of a few other metals, viz., barium, strontium, calcium, and magnesium, combine more or less eagerly with water.

**Experiment 41.**—Pass a slow current of air over fused calcic chloride contained in a U-tube, and then over a piece of sodium placed in a bulb-tube (comp. Fig. 26), and apply a gentle heat till the sodium bursts into flame. Remove now the lamp, as the combustion goes on without the application of external heat. When it has ceased, the sodium will be found to have been converted into a white powder, which attracts moisture very rapidly from the air. On moistening it with a little water it gets very hot, and is rapidly dissolved to a colourless liquid, which, when concentrated enough, corrodes the skin, whilst in a

dilute state it produces a peculiar soapy feeling when rubbed between the fingers. The liquid has a soapy disagreeable taste and a peculiar smell. A minute drop of the liquid turns a red litmus solution instantaneously blue, *i.e.*, it restores the natural blue colour of a litmus solution reddened with a drop of very dilute sulphuric acid. This is due to what is called the *alkaline* property of soda, a property pertaining also to various other metallic oxides, especially to potassa.

These oxides are called alkalis, from *Kali*, the name given by the old alchemists to the ashes of plants (potashes). Hence also the name *Kalium*, used by German chemists instead of potassium, and *Kali* in place of the oxide or potassa.

**Experiment 42.**—Burn a little magnesium wire and place the oxide of magnesium, or magnesia, on moistened red litmus-paper, or on yellow turmeric-paper. It is sufficiently soluble to change the portion of the litmus-paper with which it comes in contact to a blue colour, or that of the turmeric-paper to a red-dish brown.  $MgO$  is soluble only in about 50,000 parts of water.

**Experiment 43.**—Aluminium, except in the form of very thin leaf, becomes only superficially oxidized when heated in air or oxygen. On placing some aluminium-leaf in a jar containing oxygen, and touching the metallic leaf with a glowing splinter of wood, the aluminium burns with a sudden flash of dazzling white light. Put some of the white oxide formed on moistened litmus-paper. The paper remains unacted upon, showing that the oxide of aluminium, or alumina, is not soluble in water.

No action is observed if some other metallic oxides, *e.g.*, the oxides of iron, zinc, copper, be placed on litmus-paper. There are only comparatively few *metallic oxides* which are soluble in water, the greater number being insoluble; they neither corrode the skin nor exert any perceptible action upon vegetable colouring matters, and yet a remarkable analogy is perceptible in their chemical composition and deportment.

There is another class of oxides, *viz.*, most of the *oxides* of the *non-metallic elements*, which differ greatly in properties from, and are chemically opposed to the oxides which the metals form. We have already seen that the oxides of the elements sulphur and phosphorus combine freely with oxygen (comp. Exp. 22 and 23), and form oxides which are readily soluble in water, the solution possessing a sour or *acid* taste. We meet with acid bodies in fruits (*e.g.*, red currants, lemons, apples, &c.), in wine, in sour beer, etc. The acid taste of these substances is owing to a few so-called organic acids, such as citric, tartaric, malic, and acetic acid, or vinegar. Mineral substances, such as phosphorus and sulphur, by



FIG. 36.

combining with oxygen and water, form acid bodies which are readily distinguishable from the acids just mentioned by their intensely sour and burning taste. They instantaneously turn blue litmus solution *red*. Other non-metallic elements, with the sole exception of fluorine, are likewise capable of forming with oxygen compounds which are for the most part soluble in water, and constitute, when so dissolved, powerful acids.

**Experiment 44.**—Add slowly and cautiously, by means of a pipette, (Fig. 36) some dilute sulphuric acid to an alkaline liquid—a dilute solution of soda—tinted blue with a solution of litmus till a point is reached when the blue colour disappears and the liquid becomes red. One drop of the alkaline liquid restores the blue colour, or one drop of the acid liquid turns the blue solution red. There must, however, be a point at which the two fluids may be so mixed as to completely *neutralize* each other, *i.e.*, at which the solution neither turns blue litmus-paper red, nor red litmus-paper blue. This neutral point can be readily ascertained.

The compound produced by the action of an acid upon an alkali constitutes what is usually called a *salt*.\* The solid oxides of zinc, iron, copper, when treated with an acid liquid, such as a solution of sulphuric acid, dissolve readily; a point is reached, however, at which no more oxide dissolves, when, in fact, the acid body has become neutralized by the metallic oxide, and when a single drop of an alkaline liquid, *e.g.*, soda, will turn the solution blue. It is evident, then, that an acid may be neutralized by the alkaline solution of a metallic oxide, as well as by a solid oxide, devoid of any reaction and insoluble in water, and *salts* in general may be formed by the mutual action of an acid upon certain metallic oxides termed *bases*.† Such bases are for the most part the mono- or protoxides, and in a few cases the suboxides of the metals, also termed *basic* or *salifiable oxides*, having the formula  $R_2O$  or  $RO$ , a few only being combined in the proportion of two of the metal to three of oxygen, forming the so-called sesquioxides of the general formula,  $R_2O_3$  ( $R$  standing for metal). The terminals *ous* and *ic* are now generally used, when a metal forms two basic oxides, containing different proportions of oxygen. Copper, *e.g.*, forms two basic oxides,  $CuO$ , or cupric, and  $Cu_2O$ , or cuprous oxide. Iron forms two well-defined salifiable oxides,  $FeO$ , or ferrous, and  $Fe_2O_3$ , or ferric oxide, &c.

Some metals are capable of forming other oxides, besides the one or two so-called basic oxides already enumerated. Lead and manganese, *e.g.*, form oxides of the formula  $RO_2$ , viz., manganic dioxide, or black oxide of manganese,  $MnO_2$ , and plumbic dioxide,  $PbO_2$ , which are usually termed *indifferent* oxides, because they do not enter into chemical combination with acids without first undergoing decomposition into lower oxides of the formula  $RO$ . The intermediate oxides of the formula  $R_2O_3$  are mostly weak bases which frequently play the part of weak acid bodies towards strong bases, or towards a salifiable oxide of the same metal. Higher metallic oxides of the formula  $RO_3$ , such as  $MnO_3$ ,  $CrO_3$ , etc., act like true *acids*; they combine with bases and form salts.

The following is a list of some of the more important basic or salifiable oxides. The asterisk indicates the oxides which occur more or less abundantly in nature. Most metallic oxides are insoluble in water.

\* A definition of the term salt will be given hereafter.

† As most of the bases insoluble in water form, with acids, salts which are acid to test-paper, it is frequently advisable, in preparing such salts, to use slight excess of the insoluble base, and to filter off before crystallising the salt.

TABLE OF THE MOST IMPORTANT BASIC (OR SALIFIABLE) METALLIC OXIDES.

Lower, or —ous Oxides.	Higher, or —ic Oxides.
—	OK <sub>2</sub> , potassa† (potassic oxide).
—	ONa <sub>2</sub> , soda (sodic oxide).
—	BaO, baryta (baric oxide).
—	SrO, strontia (strontic oxide).
—	CaO, lime (calcic oxide).
—	MgO,* magnesia (magnesian oxide).
—	( <i>Periclase.</i> )
[CrO, chromous oxide.]	Al <sub>2</sub> O <sub>3</sub> ,* alumina (aluminic oxide).
FeO, ferrous oxide.	Cr <sub>2</sub> O <sub>3</sub> ,* chromic oxide.
MnO, manganous oxide.	( <i>In chrome iron ore.</i> )
CoO, cobaltous oxide.	Fe <sub>2</sub> O <sub>3</sub> ,* ferric oxide.
NiO, nickelous oxide.	( <i>Red hematite.</i> )
—	Mn <sub>2</sub> O <sub>3</sub> ,* manganic oxide.
—	( <i>Braunite.</i> )
—	[Co <sub>2</sub> O <sub>3</sub> , cobaltic oxide.]
Cu <sub>2</sub> O,* cuprous oxide.	[Ni <sub>2</sub> O <sub>3</sub> , nickelic oxide.]
( <i>Red copper ore, or ruby ore.</i> )	ZnO,* zinc oxide.
Hg <sub>2</sub> O, mercurous oxide.	( <i>Red zinc ore.</i> )
Bi <sub>2</sub> O <sub>3</sub> ,* bismuthous oxide.	CdO, cadmic oxide.
( <i>Bismuth ochre.</i> )	PbO, plumbic oxide.
[Sb <sub>2</sub> O <sub>3</sub> ,* antimonious oxide.]	CuO, cupric oxide.
( <i>White antimony.</i> )	HgO, mercuric oxide.
SnO, stannous oxide.	—
PtO, platinous oxide.	—
—	SnO <sub>2</sub> ,* stannic oxide.
—	( <i>Tinstone.</i> )
—	PtO <sub>2</sub> , platinic oxide.
—	[Au <sub>2</sub> O <sub>3</sub> , auric oxide.]
—	OAg <sub>2</sub> , argentic oxide.

**Summary.**—*Natural waters are more or less impure. They contain certain gases, together with soluble organic and mineral matter. Rain water is the purest natural water. Waters containing large quantities of gaseous or mineral matter are called mineral waters (acidulous, chalybeate, hepatic waters). Pure water can be obtained artificially by the direct combination of hydrogen and oxygen, or by a process of distillation (vaporisation) and condensation.*

**Salts** are formed in general by the mutual action of an acid upon certain metallic oxides, called **basic** or **salifiable oxides**.

† The old special names for some of the more important oxides (at one time looked upon as elementary bodies) are still retained by chemists.

## CHAPTER VIII.

**SULPHUR—Its Occurrence and Properties. ALLOTROPIC STATE OF MATTER. DIMORPHISM. SYNTHESIS OF SULPHUROUS ANHYDRIDE. SULPHURETTED HYDROGEN. METALLIC SULPHIDES.**

OXYGEN is one of the most widely diffused elements in nature; it forms a most important constituent of a great portion of inorganic or mineral nature, and is likewise of paramount importance in the animal and vegetable economy. We have seen that it combines chemically with other elements—often with great energy—and that it forms compounds of a *well defined* chemical character.

No other element equals oxygen in this respect. Many, especially the metals, possess only a limited combining power, and among the metalloids there are only two, sulphur and chlorine, which, if we merely consider their power of forming well characterized inorganic chemical compounds with other elements, are of like importance.

*Sulphur* is at the ordinary temperature a solid body of yellow colour. It occurs in nature more or less pure in the *free* state, particularly in volcanic regions, *e.g.*, in Sicily and other places. It may be purified by *distillation* from any mineral non-volatile ingredients with which it occurs mechanically mixed. By far the greater quantity of sulphur is, however, found in nature in the *combined* state, especially with metals (as blende and pyrites).

Combined with lead it furnishes the well known mineral *galena*, with zinc the brown mineral *zinc blende*, with iron the yellow brassy looking mineral known as *iron pyrites*. Combined with oxygen and water, it forms an acid, known as sulphuric acid, which is sometimes met with in waters from volcanic regions, or which when combined with bases forms salts known as *sulphates*, the most important of which are the sulphates of the metals calcium (*gypsum* and *anhydrite*), barium (*heavy spar*), magnesium (*Epsom salts*), sodium (*Glauber's salt*), and others. Several of the soluble sulphates are also found in most springs and river waters. In combination with hydrogen, it occurs in sulphurous or hepatic springs.

It enters likewise into the composition of many plants, and forms a constituent of many vegetable and animal substances, such as oil of mustard, of onions, of garlic, white of egg (albumin), muscle, casein, gall, hair, and many others. In commerce it is commonly obtained in the form of *flowers of sulphur* or *roll sulphur* (brimstone).\*

\* Specimens of native sulphur, of flowers of sulphur, and roll sulphur; of various metallic sulphides and sulphates should be examined by the student.



The *physical* properties of sulphur are of considerable interest. Sulphur is not soluble in water, but can be dissolved to a slight extent in ether, or hot alcohol; it is, however, readily soluble in oil of turpentine, benzol, or carbonic disulphide,  $\text{CS}_2$ —a volatile liquid—analogueous in composition to carbonic dioxide,  $\text{CO}_2$ .

**Experiment 45.**—Introduce some powdered sulphur into carbonic disulphide, and warm gently by plunging the flask into warm water; the sulphur dissolves readily (100 parts of  $\text{CS}_2$  dissolve 73 of sulphur). Pour out into a warm evaporating dish, and allow the carbonic disulphide to evaporate spontaneously. *Orthorhombic-octahedral* crystals of sulphur are obtained which are identical with the sulphur crystals observed in native sulphur.

**Experiment 46.**—Heat a few pieces of roll sulphur in a small beaker or crucible imbedded in warm sand on a sand-bath. Without first becoming soft or pasty the sulphur is seen to pass at once from the solid to the liquid state, and to form a clear amber yellow liquid; the pieces of unmelted sulphur remain at the bottom of the glass vessel, being, unlike ice, heavier than the liquid sulphur; or, in other words, sulphur on melting expands and occupies a larger space in the liquid state. Allow the thoroughly liquefied sulphur to cool until a solid crust forms on the surface. Pierce with a glass rod two holes through the crust near the edge on opposite sides, and pour out through one hole the still liquid sulphur, the other hole serving for the admission of air. When the mass is quite cold, remove the solid crust carefully with a knife.



FIG. 37.—PRISMATIC SULPHUR CRYSTALS.

slightly elastic at first, but become rapidly brittle and opaque; they acquire then a somewhat lighter colour, and at the common tem-

A network of long transparent honey-like *prismatic* needles, will be left behind, as seen in Fig. 37, which belong to a different crystallographic system, viz., the monoclinic system. Their specific gravity, 1.98, differs likewise from that of the orthorhombic octahedral crystals which have the specific gravity 2.05. The respective fusing points are  $120^\circ$  and  $115^\circ$  C. This variety of sulphur is insoluble in carbonic disulphide. The needle-shaped crystals are

perature they pass slowly, more rapidly at a higher temperature, back to the first or octahedral variety, and become soluble in carbonic disulphide.



FIG. 38.—DISTILLATION OF SULPHUR.

**Experiment 47.**—When sulphur is heated in a retort, it passes from the solid to the liquid, and lastly to the gaseous state. Flowers of sulphur can be heated over boiling water in an open vessel, e.g., a porcelain dish, without melting, it merely agglutinates; at  $111.5^\circ$  C., however, it melts to a honey-like liquid; on heating somewhat more strongly (to  $250^\circ$  or  $260^\circ$  C.) the colour changes to red brown, almost black, and the liquid becomes very viscid, so that the open vessel may be turned upside down without any of the liquid sulphur running out. If sulphur be heated in a retort (Fig. 38), the

same changes will be observed, and if the application of heat be continued longer no further change of colour is seen, but the sulphur becomes less viscid, and begins to sublime, and at about  $440^{\circ}\text{C}$ . it boils and distils. When the liquid sulphur is allowed to drop into water, threads may be obtained of a pure pale amber colour, by regulating the temperature carefully. The strings of distilled sulphur remain for several days quite soft and elastic, but become gradually hard, opaque, and brittle. This third variety of sulphur also called *viscid*, *plastic* or *amorphous* sulphur (from a privative, and  $\mu\omicron\rho\phi\eta$  form) in distinction from the two crystalline varieties, is insoluble in carbonic disulphide, and passes slowly back into the soluble varieties, rapidly when heated to about  $100^{\circ}\text{C}$ . The change becomes then so sudden, that the temperature rises speedily from  $100^{\circ}\text{C}$ . to  $110^{\circ}\text{C}$ .

The explanation of these different crystalline forms may be sought in the different states of tension produced by the different temperatures at which the sulphur molecules rearrange themselves, when passing from the liquid to the solid state. Bodies which possess the power of crystallising under varying conditions in forms belonging to two different crystallographic systems, are called *dimorphous bodies*, and the property itself is called *dimorphism*.

The vapour of sulphur is brownish yellow. Heated to about  $500^{\circ}\text{C}$ ., it is 6.654 times heavier than air, or 96 times heavier than hydrogen. The specific gravity of the sulphur vapour does, however, not remain constant, but decreases, at higher temperatures, till, at  $860^{\circ}\text{C}$ ., it is only 2.21 times heavier than air, or 32 times heavier than hydrogen. After this (between  $860^{\circ}$  and  $1040^{\circ}\text{C}$ .) it remains constant.

Two rare elementary bodies, Selenium and Tellurium, which resemble sulphur in most of their properties, show at low temperatures similarly abnormal vapour densities. The explanation of this is that the vapours of many bodies behave like true gases only at temperatures far higher than the temperature at which they pass from the liquid to the gaseous condition.

Octahedral, prismatic and plastic or amorphous sulphur, are merely three modifications of one and the same element. A fourth may be obtained by dissolving the elastic strings of viscid sulphur, after they have again become hard, in carbonic disulphide, when a grey insoluble *amorphous powder* is left.

The property which elementary matter, such as sulphur and a few other elements exhibit, of assuming forms physically differing from each other in crystalline structure, specific gravity, fusibility and solubility, is termed the *allotropic* state of matter. Ozone, *e.g.*, is viewed as the allotropic form of oxygen. The following table shows the allotropic modifications of sulphur:—

	Sp. gr.	Fusing points.	Solubility in carbonic disulphide.
1. Octahedral.....	2.05	115° C.	Soluble.
2. Prismatic .....	1.98	120° C.	{ Insoluble before its transformation.
3. Plastic .....	1.95	{ Are converted into the octohedral modification.	
4. Amorphous powder..	1.95		{ Insoluble.

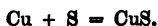


The molecular weight of  $\text{SO}_2$  is  $32 + 16 \times 2 = 64$  and 1 litre must weigh 32 times as heavy as 1 litre of hydrogen or  $32 \times .0896 \text{ grm.} = 2.8672 \text{ grms.}$

Nearly all metals are capable of uniting directly with sulphur, when heated with it, or when the vapour of sulphur is passed over the ignited metal. The metal mercury alone combines with sulphur in the cold, on account of its being a liquid at the ordinary temperature.

*Sulphur forms with Metals Sulphides.*

**Experiment 49.**—*Cupric sulphide* may be formed by heating together sulphur and copper turnings in a flask (Fig. 40). The sulphide so obtained is a black hard substance insoluble in water—



Native copper sulphides are found in Cornwall and other places.

**Experiment 50.**—Heat in a test-tube (Fig. 41) a little sulphur till the sulphur vapour fills the greater part of the tube, then introduce finely-granulated

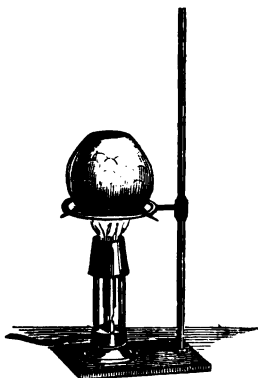


FIG. 40.—PREPARATION OF CUPRIC SULPHIDE.

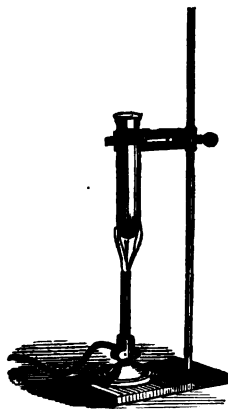
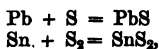


FIG. 41.—PREPARATION OF STANNOUS SULPHIDE.

lead or tin, in small quantities at a time, and heat it still more. Combination between the metal and the sulphur takes place. A sulphide of lead or tin is formed according to the equations:—

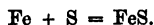


the plumbic sulphide being left as a non-crystalline, dull-black mass; the stannous sulphide as a greyish-black mass.

Lead is found in nature chiefly in combination with sulphur as *Galena*,  $\text{PbS}$ . Tin occurs most frequently as oxide, but likewise as sulphide (together with copper, iron, and zinc).

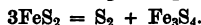
**Experiment 51.**—A thin plate of wrought-iron (not cast-iron) is heated over a Bunsen lamp to white heat, and the heated part rubbed over with a piece

of roll-sulphur. Combination between the metal and the sulphur takes place. A ferrous sulphide peels off, and the plate appears as if burnt through. The sulphide is black and insoluble in water—



The natural compounds of sulphur and iron, such as *iron pyrites*, are of considerable interest.

**Experiment 52.**—When iron pyrites,  $\text{FeS}_2$ , is heated in a test-tube or a piece of combustion-tube closed at one end, out of contact with the air, it parts with one-third of its sulphur. The change is expressed by the equation—



The sulphur sublimes and condenses in the upper part of the test-tube or ignition-tube, in orange-coloured drops, which solidify on cooling into yellow masses of solid sulphur.

**Experiment 53.**—One part by weight of sulphur and about six parts by weight of mercury (*i.e.*, atomic weights of sulphur = 32, and of mercury = 200) are rubbed together in a mortar. The little globules of mercury gradually disappear and a black powder is obtained. A partial combination takes place when the mercury and sulphur are rubbed together for several hours. As rubbing alone cannot, however, unite mercury and sulphur thoroughly, the black mass is cautiously heated in a porcelain dish or crucible, when further chemical combination takes place with slight explosions, a clear instance of the difference between mere mechanical mixture and chemical combination. Mercury and sulphur form mercuric sulphide. A similar reaction takes place when sulphur is melted, and five to six times its weight of mercury gradually stirred into it, till the sulphur begins to get viscid. Combination takes place accompanied by a flash of light and a slight report, and not unfrequently some of the mixture is violently ejected from the crucible. The mass which is left is dark-red. When cold it may be pulverized, and on mixing it with a little sulphur and heating in a flask with a long neck loosely closed with a conical piece of charcoal, the mercuric sulphide sublimes as a fine red powder called *cinnabar*.

Cinnabar is also found as a mineral. It is insoluble in water.

#### *Sulphur combines likewise with Metalloids.*

The compound which it forms when burning in air or oxygen, *viz.*, sulphurous anhydride gas, has already been noticed. Another gaseous compound of sulphur is of great importance, *viz.*, the compound which it forms with hydrogen, called sulphuretted hydrogen, or hydric sulphide. These two elements combine directly with each other; but only under exceptional conditions.

**Experiment 54.**—Treat some ferrous sulphide\*—(or any other sulphide of the same group of metals)—with dilute hydrochloric acid or sulphuric acid in a generating apparatus† (Fig. 42), consisting of a tubulated glass cylinder (known

\* Native iron pyrites ( $\text{FeS}_2$ ) cannot be employed, because it is not acted upon by dilute hydrochloric or sulphuric acid. The ferrous sulphide ( $\text{FeS}$ ) is prepared by fusing in a Hessian crucible, heated in a fire, a mixture of 7 parts of iron filings or turnings and 4 parts of sulphur (*i.e.*, atomic weights of iron = 56 and sulphur = 32).

† This apparatus may obviously be employed also for producing a constant current of hydrogen, by charging it with granulated zinc. By shutting off the screw-clamp, placed on the delivery-tube, the acid can at any time be forced back again into the doubly tubulated bottle, and the evolution of the gas made to cease almost instantaneously.

by the French name *eprouvette*) which is charged with the ferrous sulphide (in moderate sized lumps) in the manner shown in Fig. 42. A small perforated disk of sheet lead placed just above the narrow part of the cylinder prevents the

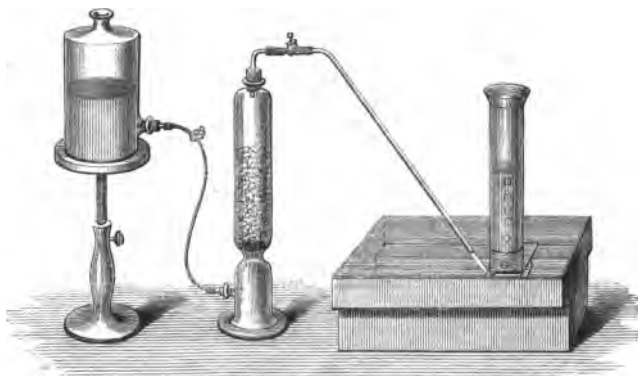
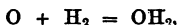


FIG. 42.—PREPARATION OF SULPHURETTED HYDROGEN.

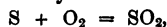
sulphide from falling to the bottom. The doubly tubulated bottle on the left hand side is charged with the dilute acid, and on slightly opening the screw clamp which closes the india-rubber tube, as well as the clamp which shuts off the delivery-tube, the acid flows into the lower (empty) part of the *eprouvette*. As soon as it reaches the ferrous sulphide, a steady current of a colourless gas is evolved, possessing a most foetid odour—



Sulphuretted hydrogen may be collected over tepid water, and several cylinders may be filled with the gas, as shown in Fig. 42. Close the cylinders under water with a greased glass plate before removing them from the pneumatic trough, and set them aside for experiment. On removing the glass plate and applying a light to the mouth of the cylinder, the sulphuretted hydrogen gas bursts into flame and burns (where it is in contact with the air) with a fine bluish flame, and partial separation of sulphur, which deposits on the sides of the cylinder. Sulphuretted hydrogen, like hydrogen, is thus a combustible gas. The hydrogen is burnt or oxidized into water—



and the sulphur into sulphurous anhydride—



the presence of which makes itself rapidly perceptible by its pungent and suffocating odour.

The combustibility of the gas may likewise be illustrated in a striking manner by burning sulphuretted hydrogen from a jet in the manner illustrated in Experiment 6. The water which condenses on the cold bell-jar will be found strongly acid to the taste and to litmus paper, since the sulphurous anhydride combines with the water, and yields a weak solution of sulphurous acid. By moistening another bell-jar with a few drops of a strong solution of ammonia, and holding it over the jet of burning sulphuretted hydrogen, white clouds are formed, consisting of a compound of sulphurous acid with ammonia.

## 58 VOLUMETRICAL COMPOSITION OF SULPHURETTED HYDROGEN.

**Experiment 55.**—Burn a little sulphur in a glass cylinder, and invert the cylinder containing the sulphurous anhydride, which is formed by the combustion of the sulphur in air over another cylinder filled with sulphuretted hydrogen gas (Fig. 43) ; withdraw the glass-plates ; the two gases diffuse, react, and mutually destroy each other ; the oxygen of the sulphurous anhydride unites with the hydrogen of the sulphuretted hydrogen, and sulphur is deposited, thus :—



(A secondary reaction takes place giving rise to the formation of a little pentathionic acid.)

**Experiment 56.**—Into another cylinder filled with sulphuretted hydrogen introduce a piece of delicate blue litmus-paper, moistened with distilled water ; the blue colour changes to red.

Sulphuretted hydrogen is a feeble acid, also called *hydrosulphuric acid*, and when acting upon bases forms true salts, the *sulphides*, sometimes called *hydrosulphates*.

**Experiment 57.**—Moisten some strips of filtering paper with a solution of sugar of lead, and hang up to drain. Plunge a strip of the moist lead-paper thus prepared into a cylinder filled with sulphuretted hydrogen gas. The paper is instantaneously blackened, owing to the formation of a compound of the

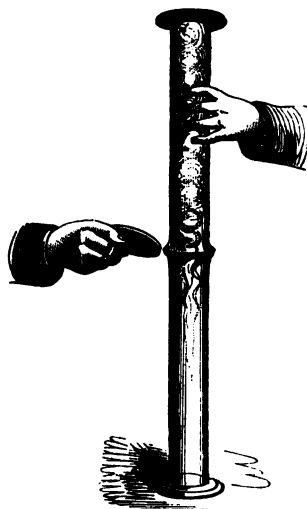


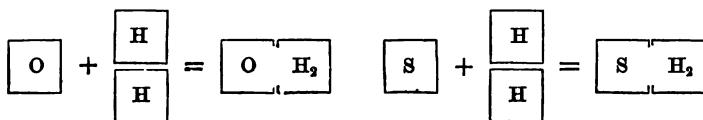
FIG. 43.—ACTION OF  $\text{SO}_2$  UPON  $\text{SH}_2$ .

sulphur with the metal lead, viz., plumbic sulphide,  $\text{PbS}$ .

The presence of sulphuretted hydrogen in crude coal-gas, or in the exhalations from drains, cess-pools, can in this manner readily be demonstrated.

When sulphuretted hydrogen is inhaled in somewhat large quantities it acts like a poison. Small animals die in an atmosphere containing as little as  $\frac{1}{1000}$  to  $\frac{1}{1500}$  of this poisonous gas. It is found wherever decomposition of organic compounds containing sulphur takes place, e.g., in sewers. Cold water absorbs from three to four times its volume of this gas ; and a solution of sulphuretted hydrogen in water forms one of the most important reagents in the laboratory. It is, however, rapidly decomposed when left in contact with air, finely divided white sulphur being precipitated.

If we examine into the combination by volume which took place between sulphur and hydrogen, we have no difficulty in recognising a resemblance between the constitution of water,  $\text{OH}_2$ , and that of sulphuretted hydrogen,  $\text{SH}_2$ . The latter gas may in fact be viewed as sulphur water, or water in which the atom (or volume) of oxygen has been replaced by an atom (or volume) of sulphur.



Its molecular weight is  $32 + 2 = 34$ . One litre of sulphuretted hydrogen compared with the volume unit (one litre of hydrogen) weighs 17 times as much, or  $17 \times .0896 = 1.5232$  gm. The specific gravity of sulphuretted hydrogen compared with hydrogen is therefore 17, and when compared with air 1.199.

The great affinity which metals possess for sulphur enables us to separate most metals from their saline solutions in the form of sulphides.

**Experiment 58.**—Dissolve a few crystals of the following well-known salts in distilled water (solutions 2 and 3, with the addition of a little ammonia), and pass sulphuretted hydrogen gas through their solutions, using test-tubes or bottles fitted with doubly perforated corks (Fig. 44).

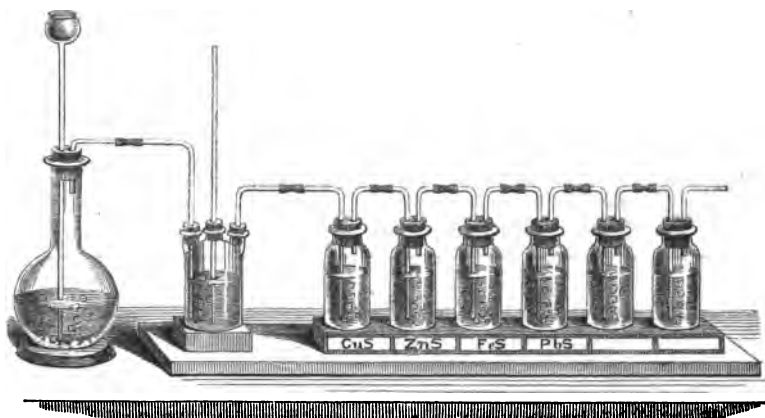


FIG. 44.

			Result.
1. Blue vitriol (or cupric sulphate)	..	..	a black precipitate,
2. White vitriol (or zincic sulphate)	..	..	a white precipitate,
3. Green vitriol (or ferrous sulphate)	..	..	a black precipitate,
4. Sugar of lead (or plumbic acetate)	..	..	a black precipitate,
5. Alum .. .. .	..	..	no precipitate,
6. Epsom salts .. .. .	..	..	no precipitate.

The sulphur of the sulphuretted hydrogen combines instantaneously with the metal, and forms a metallic sulphide—(1) Cupric sulphide,  $\text{CuS}$ ; (2) Zincic sulphide,  $\text{ZnS}$ ; (3) Ferrous sulphide,  $\text{FeS}$ ; (4) Plumbic sulphide,  $\text{PbS}$ , whilst the metals aluminium in alum, and magnesium in Epsom salts do not possess sufficient affinity for sulphur to form a sulphide in the wet way.

Most metallic sulphides (the alkaline sulphides excepted) are either insoluble or with difficulty soluble in water; and it is obvious, therefore, why a precipitate appeared, as soon as the sulphur of the sulphuretted hydrogen combined with the metals copper, zinc, iron, or lead.

The following is a list of some of the more important *metallic* sulphides, the asterisk indicating the sulphides which occur more or less abundantly in nature:—



TABLE OF THE MOST IMPORTANT METALLIC SULPHIDES.

SK <sub>3</sub> , potassic sulphide.	SAg <sub>2</sub> ,* argentic sulphide. ( <i>Silver glance.</i> )
SNa <sub>2</sub> , sodic sulphide.	SnS, stannous sulphide.
BaS, baric sulphide.	SnS <sub>2</sub> , stannic sulphide. ( <i>Tin pyrites, bell metal ore.</i> )
SrS, strontic sulphide.	PbS,* plumbic sulphide. ( <i>Galena.</i> )
CaS, calcic sulphide.	Hg <sub>2</sub> S, mercurous sulphide.
FeS, ferrous sulphide.	HgS,* mercuric sulphide. ( <i>Cinnabar.</i> )
Fe <sub>2</sub> S <sub>3</sub> , { ferric sulphide, or diferic trisulphide.	Cu <sub>2</sub> S,* cuprous sulphide. ( <i>Vitreous copper, or copper glance.</i> )
FeS <sub>2</sub> ,* ferric disulphide. ( <i>Iron pyrites, martial pyrites.</i> )	CuS,* cupric sulphide. ( <i>Indigo copper, or blue copper.</i> )
ZnS,* zinc sulphide. ( <i>Zinc blende.</i> )	Bi <sub>2</sub> S <sub>3</sub> , bismuthous sulphide. ( <i>Bismuth glance.</i> )
MnS, manganeous sulphide. ( <i>Manganese blende.</i> )	Sb <sub>2</sub> S <sub>3</sub> ,* antimonious sulphide. ( <i>Antimony glance.</i> )
CoS, cobaltous sulphide.	PtS <sub>2</sub> , platinic sulphide.
Co <sub>2</sub> S <sub>3</sub> ,* cobaltic sulphide. ( <i>Cobalt pyrites.</i> )	Au <sub>2</sub> S <sub>3</sub> ,* auric sulphide.
NiS,* nickelous sulphide. ( <i>Capillary pyrites, hair nickel.</i> )	
NiS <sub>2</sub> , nickelic disulphide.	
CdS, cadmic sulphide. ( <i>Greenockite.</i> )	

*Solution, precipitation.*—We have repeatedly seen that bodies may be dissolved in water, forming what is termed a *simple solution*. The liquid in which the solution is effected is termed a *solvent*. Water (distilled) is most frequently employed for this purpose; other solvents, e.g., alcohol, ether, chloroform, etc., are occasionally but rarely employed. A finely-divided substance dissolves more readily than a coarse powder or a crystalline body; it also, with very few exceptions, dissolves more rapidly and to a greater extent in hot than in cold water.

A solid body can be recovered from its solution by *evaporation*. This may be effected by heating the solution in a porcelain dish over a little copper water-bath (Fig. 45) or over the bare flame, by so regulating the heat as to prevent loss by spurling; or it may be recovered by modifying or removing the *solvent*; NaCl, e.g., which is soluble in water, is precipitated on the addition of concentrated hydrochloric acid; calcic carbonate dissolved in carbonic acid by the removal of the gaseous solvent on boiling; or, lastly, by the *sudden conversion of the liquid into a solid body* by the action of another body, induced by greater chemical affinity, one substance remaining in solution as a general rule.



FIG. 45.—EVAPORATION ON A WATER-BATH.

The body which is precipitated is termed the *precipitate*. It generally sinks to the bottom of the glass vessel (test-tube, etc.) on

account of its greater specific gravity. Stirring, as well as the application of heat, frequently promotes the subsidence of the precipitate. We speak of *pulverulent* (amorphous), *crystalline*, *flaky*, *curdy*, *gelatinous* precipitates, according to the appearance which they present. This and the colour of a precipitate assist materially in identifying a body.

The body which precipitates another body is called the *precipitant*.

#### QUESTIONS AND EXERCISES.

1. How does sulphur occur in nature?
2. What are the properties of sulphur—1st, at the ordinary temperature; 2nd, when heated to  $111^{\circ}\text{C}$ .; 3rd, at a temperature of  $250\text{--}260^{\circ}\text{C}$ .?
3. Define a metallic sulphide.
4. Explain what changes take place when sulphur is heated, 1st out of contact with the air, and 2nd with free access of air.
5. Describe the allotropic modifications of sulphur.
6. What is understood by *dimorphism*?
7. In what proportions by weight does sulphur combine on ignition with oxygen, and what will be the volume weight and the molecular weight of the product of combustion?
8. How would you explain the fact that no contraction of volume takes place when sulphur and oxygen combine, and how does a knowledge of the density of oxygen and sulphurous anhydride, as compared with air, enable you to prove the volume composition of  $\text{SO}_2$ ?
9. Explain the terms *roll sulphur* or *brimstone*, *flowers of sulphur*, *distilled sulphur*, *copper pyrites*, *galena*, *iron pyrites*.
10. How is cinnabar prepared?
11. Describe the preparation of sulphuretted hydrogen from ferrous sulphide, and state briefly its properties; give equations.
12. What are the products of the combustion of sulphuretted hydrogen in air? Express the changes by equations.
13. What change does a solution of sulphuretted hydrogen in water undergo when exposed to air?
14. How would you extract sulphur from iron pyrites?
15. Calculate the percentage composition of  $\text{SH}_2$ .
16. State whether the atomic weights of  $\text{SH}_2$  and  $\text{SO}_2$  are identical with the molecular weights.
17. What is the density of  $\text{SO}_2$  and  $\text{SH}_2$  compared with hydrogen, and what is the weight in grms. of one litre of the respective gases?
18. How would you demonstrate experimentally the action of  $\text{SH}_2$  upon different saline solutions, such as a solution of sugar of lead, blue and green vitriol, etc.?
19. You have given to you iron filings, flowers of sulphur, and dilute hydrochloric acid: describe accurately the different chemical changes which, in your opinion, can be produced with these materials.
20. State how you would purify a sample of *rough sulphur* containing from three to four per cent. of earthy impurities; also, how you would determine the amount of sulphur quantitatively.

## CHAPTER IX.

## CHLORINE, its Properties.—CHLORIDES.

**Experiment 59.**—When a well known mineral called *black oxide of manganese*,  $\text{MnO}_2$ , composed of one atom of the metal manganese and two atoms of oxygen, is gently heated with concentrated hydrochloric acid in a generating flask (Fig. 46), a yellowish green gas, called *chlorine*,\* is evolved, which cannot,

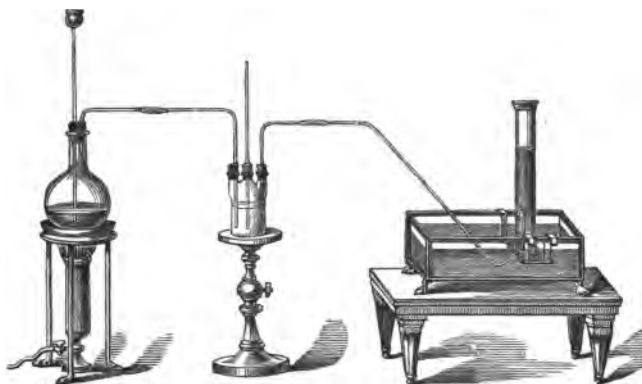
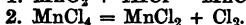
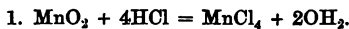


FIG. 46.—PREPARATION OF CHLORINE GAS.

even when largely diluted with air, be inhaled without danger, on account of its highly poisonous nature, and the black oxide of manganese dissolves to a yellowish coloured liquid, containing manganous chloride,  $\text{MnCl}_2$ . The reaction takes place in two stages—



Chlorine gas, like hydric sulphide, is soluble in water—cold water dissolves at  $10^\circ \text{C}$ . nearly three times its bulk of chlorine—and a solution of chlorine may be obtained by passing the gas for some time into cold water. The gas can be collected over warm water in a pneumatic trough, as seen in Fig. 46, or it may also be collected by displacement, *i.e.*, the delivery-tube is passed to the bottom of an upright glass cylinder, or test-tube, till the whole of the cylinder is filled with the yellowish green gas. The lighter air is gradually lifted out of the cylinder by the heavier chlorine. The operation of collecting a highly poisonous gas like chlorine must be carried on in a well ventilated closet. Cylinder after cylinder may thus be filled with chlorine. Absolute displacement of the air is not possible, nor is it of much consequence. The edge of the cylinder is slightly greased, and a glass plate, when gently pressed down upon the opening, effectually shuts in the gas. Chlorine cannot, like some other gases, be collected over mercury, as it acts slowly upon this metal, forming with it a soluble salt, mercuric chloride.

Chlorine gas is considerably heavier than air, its specific gravity

\* From  $\chi\lambda\omega\rho\acute{o}\varsigma$ , yellowish green.

compared with air, is 2.46, or  $\frac{2.46}{.0691} = 35.5$ , when compared with hydrogen gas.

1 litre of chlorine gas therefore weighs 35.5 criths, or  $35.5 \times .0896 \text{ grm.} = 3.1808 \text{ grms.}$  It is a two volume gas  $\boxed{\text{Cl} \quad \text{Cl}}$ , and its molecular weight is  $2 \times 35.5 = 71$ .

**Experiment 60.**—Introduce into a cylinder charged with chlorine gas flowers of various colours, a strip of litmus-paper, a piece of moistened cotton print, printed and written slips of paper, and cover over with the glass plate. The colours of the flowers disappear; violets, *e.g.*, become quite colourless; the cotton print is turned white; the ink acquires a reddish-brown appearance; the printing ink alone, or the finely divided carbon which it contains (lamp-black) remains unaffected.

This proves, then, that chlorine is a *powerful bleaching agent*. Hence its application in the arts and manufactures. Linen and cotton goods are bleached by the agency of chlorine, and paper pulp is rendered white. Silk or woollen stuffs, however, cannot be bleached by chlorine, because the fibres of these fabrics are destroyed by it. Mineral colours, in general, are not affected by it. Chlorine water bleaches equally well.

A *solution* of chlorine in water is a useful reagent in the laboratory.

**Experiment 61.**—The solution is prepared by passing a current of chlorine gas through Woulfe's bottles, as seen in Fig. 47. The contents of the Woulfe's bottle nearest to the generating flask are generally contaminated with

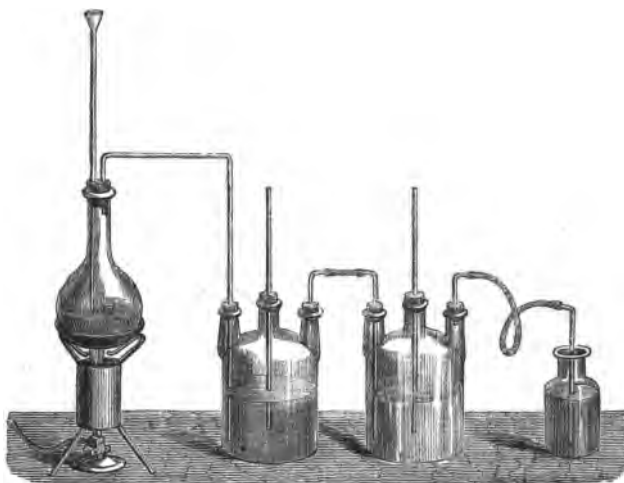


FIG. 47.—PREPARATION OF CHLORINE WATER.

some hydrochloric acid, which has been carried over by the chlorine, and are best rejected. A simpler method of making a saturated solution of chlorine con-

sists in passing the gas from the first Woulfe's bottle to a retort inverted, as seen in Fig. 48, containing cold distilled water.

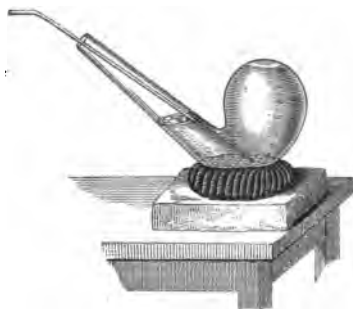


FIG. 48.

When cooled to near the freezing point of water crystals of a molecular compound of chlorine with water are formed, containing for every molecule of chlorine 10 molecules of water. Their composition is expressed by the formula  $\text{Cl}_2 \cdot 10\text{OH}_2$ . If a strong glass tube embedded in a freezing mixture be nearly filled with the crystals, and if it be then drawn out before the blowpipe flame and carefully sealed, the crystals will melt as soon as the temperature rises, and yellow oily drops of liquid chlorine subside through the water. The pressure which the chlorine exerts upon the glass tube at  $15^\circ \text{C}$ . is equal to that of four atmospheres. Liquid chlorine has a specific gravity

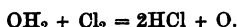
of 1.38. It does not solidify even when cooled to  $-110^\circ$ .

**Experiment 62.**—Place a cylinder filled with chlorine gas mouth to mouth with another cylinder (comp. Fig. 43) containing sulphuretted hydrogen gas. On withdrawing the glass plates with which they are covered the two gases mix, and sulphur is seen to be deposited. If the rims of the cylinders be slightly greased, they will adhere air-tight, and when detached from each other under water, the latter rushes in and speedily fills both cylinders.

This shows that the new gaseous body is soluble in water. Test the water with litmus-paper. It is *acid*. The chlorine has formed with the hydrogen a gaseous binary compound, an acid, known as *hydrochloric acid* or *hydric chloride*, according to the equation  $\text{SH}_2 + \text{Cl}_2 = 2\text{HCl} + \text{S}$ .

The action of chlorine upon sulphuretted hydrogen is analogous to that which chlorine water undergoes when exposed to sunlight.

A solution of chlorine in water has the same yellowish-green colour as the gas itself. It should be kept in the dark, as it becomes gradually decomposed when exposed to sunlight, especially to direct sunlight. The hydrogen of the water goes to the chlorine to form hydrochloric acid, which remains dissolved in the water, and the oxygen is liberated—



This action arises from the powerful affinity which chlorine has for hydrogen, an affinity which is greater than that which either of the elements oxygen or sulphur possess for that element.

The bleaching action of chlorine depends upon the same chemical change; it is an indirect process of *oxidation*.

What is done slowly by sunlight may be effected more rapidly by employing heat. The apparatus required to illustrate the reaction renders the experiment, however, more fit for the lecture room than for the laboratory.

**Experiment 63.**—Pass a slow current of steam and chlorine simultaneously through a porcelain tube, loosely filled with fragments of broken porcelain, and heated to redness in a charcoal furnace (Fig. 49). The chlorine generated in the flask provided with the funnel-tube, by the action of hydrochloric acid upon

black oxide of manganese passes through a wash-bottle, containing water, into a second flask, in which steam is generated. The small Woulfe's bottle arrests any condensed steam. The rectangularly bent glass tube leading to the porcelain

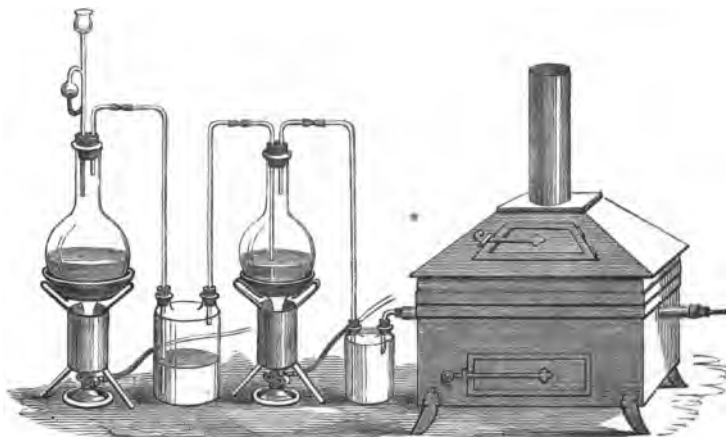
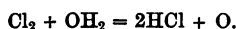


FIG. 49.—DECOMPOSITION OF STEAM BY CHLORINE.

tube should be cut off *slantingly*, and should be as *short* as possible, to prevent any drops of condensed water from being carried forward into the porcelain tube, with the imminent risk of cracking the latter. Under the influence of a strong heat, and favoured by the gaseous condition of the two bodies, the chlorine breaks up some of the steam with formation of hydrochloric acid gas, and liberation of oxygen, which can be collected from the exit-tube in the usual manner over water, rendered alkaline by a solution of sodic hydrate, in order to absorb any undecomposed chlorine, as well as the hydrochloric acid which formed. The reaction is expressed thus :—



**Experiment 64.**—Place a burning taper in a cylinder and hold a second cylinder filled with chlorine gas to the mouth of the upright cylinder, as seen in Fig. 50. As the chlorine descends the taper continues to burn with a feeble yellowish flame, and heavy clouds of smoke or soot are seen to separate.

A candle, whether made of paraffin, wax, tallow, or spermaceti, consists of carbon and hydrogen, or of carbon, hydrogen, and oxygen, in varying proportions. The chlorine acting upon the hydrogen sets the carbon free in the form of solid particles or black soot. This then proves that the white material of which candles are made contains carbon, and that chlorine has a strong affinity for hydrogen

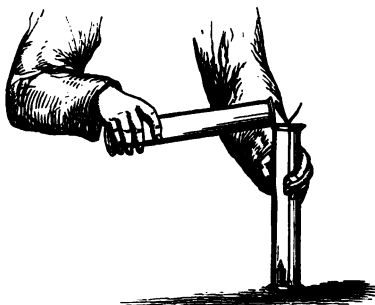
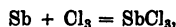


FIG. 50.

and none for carbon. The chlorine forms with the hydrogen hydrochloric acid. This can be shown by rinsing out the cylinder with a little water and testing with blue litmus paper.

**Experiment 65.**—Powder some metallic antimony very finely, and place the powder in a fine sieve sufficiently large to cover the opening of a tall and wide glass cylinder filled with chlorine gas. Shake the sieve gently. Some of the finely divided antimony falls through into the chlorine gas, and combines with it, giving rise to quite a rain of fire, and the cylinder becomes filled with thick white fumes. The chlorine gas combines directly with the metal antimony—



and the chemical change is accompanied by great heat, and the phenomenon of light. To prevent cracking the cylinder, it is well to place some white sand at the bottom.

A similar but less energetic action is observed when chlorine is made to act in a retort or tube of hard glass upon copper-leaf, or upon Dutch metal, an alloy of zinc and copper. The reaction has, however, to be started and assisted by the application of heat. Flashes of light are likewise given out during the combination of the metals with the chlorine gas. The compounds so formed are found on analysis to be composed of 1 atom of the metal to 2 atoms of chlorine, *e.g.*,  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$ .

**Experiment 66.**—Set fire to some magnesium wire and introduce the burning magnesium quickly into a cylinder filled with chlorine gas. It continues to burn with great brilliancy in the gas. The product of the combustion of magnesium in chlorine is a white powder, magnesian chloride ( $\text{MgCl}_2$ ), which on exposure to the air rapidly attracts moisture and liquefies. Test the liquid. It is neutral to test-papers.

**Experiment 67.**—Place a small piece of sodium in a deflagrating spoon; ignite the metal and plunge it rapidly into a glass jar containing chlorine. The sodium burns brilliantly in the chlorine. Take some of the white powder which is formed by the combination of the sodium with the chlorine, and dissolve it in a little water.

The solution shows no action upon either blue or red litmus-paper; it is an indifferent or neutral liquid; it tastes neither sour (acid) nor caustic (alkaline). It has the taste of common salt. In fact, *by the combination of the metal sodium and the gas chlorine, we have produced common salt*, and have proved thereby that our common table salt—*sodic chloride* ( $\text{NaCl}$ )—consists of two elementary bodies, of sodium and of chlorine.

**Nature of Metallic Chlorides.**—As all metallic chlorides, with the exception of the chlorides of platinum and gold, can be prepared like sodic chloride (and several of the metallic chlorides produced in the previous experiments, *e.g.*,  $\text{SbCl}_3$ ,  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{MgCl}_2$ ), by the *direct* combination of a metal and chlorine, they must be analogous to this well known salt, and the latter may be regarded as the representative of metallic chlorides generally. From the most remote times sodic chloride has received the name of *salt*, and has always been known as “the salt.” The same name in its generic construction is now assigned to other metallic chlorides. They are distinguished from the corresponding metallic oxides by their reaction on vegetable colours (litmus-papers). Not one metallic

chloride possesses an alkaline reaction, the chlorides of some of the heavy metals giving even an acid reaction; whilst the corresponding oxides have either a strongly alkaline (caustic) character, or show no reaction at all with litmus.

Sodic chloride is found in nature very widely distributed. From one of its sources, viz., sea-water, it is obtained by *evaporation* and *crystallization*. The so-called *mother liquor* (or concentrated saline solution from which salt has been removed by crystallisation) has been found to contain two other elementary bodies, bromine and iodine, which closely resemble chlorine in their properties. They exist chiefly in combination with magnesium, as bromide and iodide of magnesium. These elements can likewise be isolated. *Bromine*\* (symbol Br), at the ordinary temperature is a dark brownish disagreeably smelling, very poisonous liquid. *Iodine*† (symbol I) is a crystalline substance of dark steel or deep violet colour, subliming in beautiful violet vapour, when a small crystal of it is gently heated in a test-tube. These two elements, together with another elementary body, found in fluor spar, called *fluorine* (symbol F), (never isolated as yet), can likewise combine with metals, and are classed together with chlorine under the name of *halogens* or *salt formers* (from *ἅλς*, salt, and *γεννάω*, I generate). They also combine with hydrogen and form acids—gaseous like hydrochloric acid gas, and eagerly absorbed by water. These acids are called—

Hydrobromic acid (Hydric bromide)	HBr.
Hydriodic       "       (       "       iodide)	HI.
Hydrofluoric   "       (       "       fluoride)	HF.

Chlorine we have already seen combines with non-metals (metalloids) as well as with metals. Chemical combination takes place between them with great energy, mostly marked by flashes of light and evolution of much heat. Phosphorus, sulphur, and carbon form chlorides, although the latter element cannot combine directly with chlorine. A knowledge of these compounds is, however, best acquired by attending a course of lectures, since the explanation of the chemical changes involved in their formation would, to a great extent, be a mere repetition of what has already been studied. The most important compound is that which chlorine forms by *direct* combination with hydrogen.

**Experiment 68.**—A wide capacious flask (Fig. 51) is filled by downward displacement with chlorine gas. A gas-holder filled with hydrogen furnishes a steady supply of gas. A glass tube bent in the manner shown by the figure is drawn out to a jet, and connected with the delivery-tube by means of india-rubber tubing; the gas is lit, and the burning jet rapidly introduced into the flask. It continues to burn for some time with a bright blue flame. The flame dies gradually away; and on removing the delivery-tube and closing the mouth of the flask rapidly with the palm of the hand or a cork,



FIG. 51.—COMBUSTION OF HYDROGEN IN CHLORINE.

\* From *βρωμος*, a stench.

† From *ιώδης*, violet-coloured.



and introducing it, mouth downward, into cold water, and then withdrawing the hand or the cork, the water rushes into the flask and nearly fills it. Remove the flask by inserting the cork, and test its contents with litmus-paper. The liquid reddens blue litmus-paper instantaneously. This shows that it contained an *acid gas* which is *eagerly absorbed by water*. From its purely synthetical origin, it can only be hydrochloric acid gas or hydric chloride, and the liquid a very dilute hydrochloric acid solution.

That hydrogen and chlorine in hydrochloric acid gas are combined in *equal* volumes may be roughly shown synthetically by charging a strong soda-water bottle with equal volumes of these two elementary gases, and applying a light. The bottle should be well wrapped up in a thick towel, as the experiment is not free from danger, owing to the violent explosion with which the two gases combine. As the hydrochloric acid gas is so very soluble in water, and as chlorine acts upon mercury, the synthetical experiment cannot be made with accuracy.

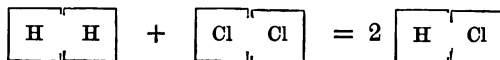
It may, however, be shown analytically by decomposing a strong solution of hydrochloric acid by means of voltaic electricity in Hofmann's apparatus (see Exp. 36) used for the electrolysis of water, but somewhat modified, as seen in Fig. 52, by substituting a flexible india-rubber tube and a small glass globe for the long tube in Fig. 30.



FIG. 52.—ELECTROLYSIS OF HYDROCHLORIC ACID.

**Experiment 69.**—Fill the apparatus (Fig. 52), instead of with water, with a concentrated solution of hydrochloric acid, and connect the wires with a voltaic battery. Hydrogen is speedily liberated at the negative pole, whilst at first scarcely any evolution of gas is observed at the positive pole, owing to the solubility of the chlorine in the acid. The decomposition should therefore be started for some time so as to allow of the liquid to become well saturated with chlorine before the two gases are collected in the two limbs of the apparatus. The pressure should also be equalized in the limbs and the movable glass-globe, for the greater the pressure the more gas remains dissolved. By opening the glass stopcocks, the gases may be discharged as long as the evolution of gas from the two electrodes is not equally strong. Having collected equal volumes of the gases separately, their properties can be readily studied. One will be found by its ready combustibility to be hydrogen; the other is non-inflammable, and possesses bleaching properties: it is chlorine.

*Properties of the gas.*—Hydrochloric acid forms a colourless transparent gas of pungent acid odour. Its combining proportions by volume may be represented as follows:—



*i.e.*, 1 molecular volume of chlorine gas on combining with a molecular volume of hydrogen, forms two molecular volumes of hydrochloric acid gas. The two gases combine without contracting.

Combination takes place with explosive violence when a mixture of hydrogen and chlorine is exposed to *direct sunlight*, slowly only when left exposed to *diffused daylight*, and not at all at the ordinary temperature when placed in darkness. The specific gravity of hydrochloric acid gas compared with air is 1.262 and compared with

$$\text{hydrogen } \frac{1.262}{.0691} = 18.25, \text{ i.e., 1 litre of hydrochloric acid weighs } \frac{1 + 35.5}{2} = \frac{36.5}{2} = 18.25 \text{ times as much as 1 litre of hydrogen}$$

or 18.25 criths, equal to  $18.25 \times .0896$  grm. or 1.6352 grm. The molecular weight of hydrochloric acid gas is 36.5. It is most eagerly absorbed by water—one litre of water is capable of absorbing 500 litres of gas at  $0^{\circ} \text{C}$ . Water so saturated fumes in the air, the vapour of the acid combining with the moisture in the air, and the liquid constitutes the ordinary commercial fuming hydrochloric acid.

Bromine, iodine and fluorine when combined with hydrogen form likewise acid liquids with water, which possess considerable interest; they will be considered more fully hereafter.

As these acids contain no oxygen, like the acids with which we have already become acquainted, they have been called *hydrogen acids* or simply *hydro-acids*, as distinguished from *oxygen* or *oxy-acids*. Oxygen then is not the only element which can by its combination with other elements form acids, as was thought at the time when this element was first discovered, and when it received the name *oxygen* or *generator of acids*. In fact, on comparing the compounds which oxygen forms with metals, such as potassium or sodium (which are perhaps only of a *basic* character, since these powerful metals neutralize and actually overpower the acidifying properties of oxygen), with the compounds which potassium and sodium form with chlorine, it is obvious, that chlorine rather deserves to be called an *acid generator*: for the compound which it forms with hydrogen is a *powerful acid*, and its compounds with potassium and sodium are neutral or indifferent bodies, the metals obviously not being capable of overpowering to the same extent the acidifying properties of chlorine as they overpower those of oxygen. This acidifying property of chlorine becomes still more apparent, when we compare some of the chlorides of the heavy metals which are strongly acid, with the corresponding oxides which are mostly quite indifferent bodies.

Metallic chlorides are soluble in water, with the exception of the chlorides of silver ( $\text{AgCl}$ ), mercurous ( $\text{Hg}_2\text{Cl}_2$ ), and lead ( $\text{PbCl}_2$ ); the latter is difficultly soluble in cold, readily soluble, however, in boiling water. Cuprous ( $\text{Cu}_2\text{Cl}_2$ ), aurous ( $\text{AuCl}$ ), and platinous chloride ( $\text{PtCl}_2$ ) are almost insoluble in water.

The following is a list of some of the more important metallic chlorides, the asterisk marking those which are found more or less abundantly in nature:—

TABLE OF THE MOST IMPORTANT METALLIC CHLORIDES.

KCl,* potassic chloride. ( <i>Stassfurth salt.</i> )	SnCl <sub>2</sub> , stannous chloride.
NaCl,* sodic chloride. ( <i>Common salt.</i> )	SnCl <sub>4</sub> , stannic chloride.
BaCl <sub>2</sub> , baric chloride.	PbCl <sub>2</sub> , plumbic chloride. ( <i>In Mendipite.</i> )
SrCl <sub>2</sub> , strontic chloride.	Hg <sub>2</sub> Cl <sub>2</sub> , mercurous chloride. ( <i>Calomel.</i> )
CaCl <sub>2</sub> ,* calcic chloride. ( <i>In many mineral waters.</i> )	HgCl <sub>2</sub> , mercuric chloride. ( <i>Corrosive Sublimate.</i> )
MgCl <sub>2</sub> ,* magnesian chloride. ( <i>In sea water.</i> )	Cu <sub>2</sub> Cl <sub>2</sub> , cuprous chloride.
Al <sub>2</sub> Cl <sub>3</sub> , aluminic chloride.	CuCl <sub>2</sub> , cupric chloride.
Cr <sub>2</sub> Cl <sub>3</sub> , chromic chloride.	BiCl <sub>3</sub> , bismuthous chloride.
FeCl <sub>2</sub> , ferrous chloride.	SbCl <sub>3</sub> , antimonious chloride.
Fe <sub>2</sub> Cl <sub>3</sub> , ferric chloride.	PtCl <sub>2</sub> , platinumous chloride.
ZnCl <sub>2</sub> , zincic chloride.	PtCl <sub>4</sub> , platinic chloride.
MnCl <sub>2</sub> , manganous chloride.	AuCl, aurous chloride.
CoCl <sub>2</sub> , cobaltous chloride.	AuCl <sub>3</sub> , auric chloride.
NiCl <sub>2</sub> , nickelous chloride.	AgCl, argentic chloride. ( <i>Hornsilver.</i> )
CdCl <sub>2</sub> , cadmic chloride.	

It will be seen from this table that very few chlorides only are found in nature, but that they contain just those metals (K, Na, Ca, Mg) which are, for the most part, not met with in the form of native oxides or sulphides.

## QUESTIONS AND EXERCISES.

1. How is chlorine prepared? Give equations.
2. Describe briefly the properties of chlorine.
3. Explain the bleaching action of chlorine.
4. State how chlorine water becomes decomposed when exposed to sunlight, or when it is acted upon by sulphuretted hydrogen.
5. Define a metallic chloride. Describe instances of the direct combination of chlorine with metals, and express the chemical changes by equations.
6. Show in what respect metallic chlorides differ from metallic oxides.
7. Explain the meaning of the terms *chlorine*, *bromine*, *iodine*, and *fluorine*.
8. Enumerate briefly the distinguishing features of chlorine, bromine, and iodine.
9. Explain the terms *halogen*, *hydro-acid*, *hydric chloride*.
10. How is hydrochloric acid gas prepared, and what are its most characteristic properties?
11. What is the volume weight and the molecular weight of chlorine and of hydrochloric acid gas?
12. What is the weight of one litre of Cl and of a litre of HCl in grammes?
13. You have given to you black oxide of manganese, concentrated hydrochloric acid, and metallic antimony: state what chemical changes you can produce with these materials.
14. The density of hydrogen gas compared with air is .0691, that of chlorine gas 2.46; find, from these figures, the atomic weight of chlorine.
15. Calculate the percentage composition of HCl and of NaCl.

## CHAPTER X.

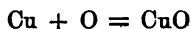
APPLICATION of the THEORY of CONSTANT  
CHEMICAL COMBINING PROPORTIONS.

SYMBOLIC formulæ have hitherto served—

- 1st. To represent bodies, elementary or compound.
- 2nd. To illustrate in the briefest manner, the play of chemical affinities, the breaking up of existing chemical compounds, and the building up of new bodies.

They serve, however, another and most important purpose, for they also bear, as has been already remarked (Chapter VI), the impression of the respective atomic weights of the element or compound body which they denote.

Equations illustrating chemical changes express likewise the relative *quantities* of the elements which form the compounds acting upon each other, or which take part in the changes, and hence they furnish the basis for *quantitative* chemical calculations. Thus the formation of cupric oxide by the action of oxygen on copper is expressed by the equation—



which conveys to the mind at the same time the idea that one atom of copper combines with one atom of oxygen to form the molecule cupric oxide. The atomic weight of copper being 63·5, that of oxygen 16, our equation tells us, by a process of simple substitution, that 16 parts by weight of oxygen combine with 63·5 parts by weight of copper, and that the two together must form 79·5 parts by weight of cupric oxide. The symbolic equation is thus transcribed arithmetically—

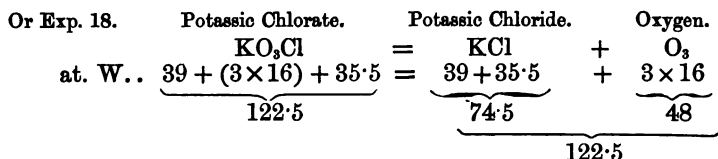
$$63\cdot5 + 16 = 79\cdot5$$

and it is easy to calculate the quantities of copper and oxygen involved in the formation of a given quantity of cupric oxide, and the quantity of cupric oxide obtained from known quantities of copper and oxygen.

It will be found useful, for the sake of practice, to transcribe, both symbolically and arithmetically, some of the reactions already studied, *e.g.*, the reactions involved in Experiments 7, 8, 11, 12, 13, 14, 15, 18, 22, 23, 24, 31, 40, 49, 50, 51, 52, 53, 54, 55, 59, 62, 63, 65, 66, 67, 68. This may be done somewhat in the following manner :—

Exp. 7.	Mercury.		Oxygen.		Mercuric Oxide.
	Hg	+	O	=	HgO
at. W..	200	+	16	=	$\underbrace{200 + 16}_{216}$

or expressed in words:—200 parts by weight (pounds, ounces, grains, grammes, etc.), of the metallic element mercury can combine, under favourable conditions, with 16 parts by weight of the gaseous non-metallic element oxygen, to furnish 216 parts by weight of solid mercuric oxide.



or in words:—122.5 parts by weight of potassic chlorate furnish 74.5 parts by weight of the salt potassic chloride, and 48 parts by weight of oxygen gas.

Questions such as the following will now readily be answered by a mere calculation of rule of three:

1. How much Cu combines with a given quantity of O?
2.     "     O                     "     Cu?
3.     "     CuO can be formed from     "     Cu?
4.     "     Cu is contained in a     "     CuO?
5.     "     O                     "     CuO?

If we wish to know—1st, how much cupric oxide, CuO, we can get by the oxidation of 100 grains of copper, we have—

$$63.5 : 79.5 :: 100 : x.$$

Atomic weight    Weight of a molecule  
of copper.        of cupric oxide.

*Ans. = 125.19 grs. of CuO.*

2. How much copper is left when 100 grains of cupric oxide, CuO, are reduced in a current of hydrogen gas?

$$79.5 : 63.5 :: 100 : x.$$

Molecular weight    Atomic weight of  
of cupric oxide.     of copper.

*Ans. = 79.87 grs. of Cu.*

3. How much mercury, Hg, is required to form 20 grms. of mercuric oxide, HgO?

$$216 : 200 :: 20 : x.$$

Molecular weight    Atomic weight  
of HgO.             of Hg.

*Ans. 18.51 grms.*

4. How much iron, Fe, has to be taken to produce 100 lb. of ferrous sulphide, FeS?

$$88 : 56 :: 100 : x.$$

Molecular      Atomic  
weight of FeS. weight of Fe.

*Ans.* 63.63 lb.

5. How much ferrous sulphide can be obtained by the combination of iron with 50 lb. of sulphur?

$$32 : 88 :: 50 : x.$$

Atomic      Molecular  
weight of S. weight of FeS.

*Ans.* 137.5 lb.

6. How much hydrogen by weight, and by volume (in litres), is required to reduce 25 grms. of cupric oxide, CuO, to metallic copper?

$$79.5 : 2 :: 25 : x.$$

Molecular weight      Weight of the  
of CuO.      molecule  
                                 of H.

*Ans.* .6289 grm. of H.

On dividing .6289 grm. by the weight of one litre of hydrogen, measured at 0° and 760 mm. barometrical pressure, viz., .0896 grm., or a crith, we obtain the number of litres of hydrogen gas at the same temperature and pressure—

$$\frac{.6289}{.0896} \quad \text{Ans. } 7.01 \text{ litres of H.}$$

7. How much sulphurous anhydride, SO<sub>2</sub>, is obtained by the combustion of 10 grms. of sulphur in oxygen gas—1st, by weight; 2nd, by volume (litres)?

$$32 : 64 :: 10 : x.$$

Atomic      Molecular  
weight of S. weight of SO<sub>2</sub>.

*Ans.* 20 grms. of SO<sub>2</sub>.

The volume weight of SO<sub>2</sub> is 32 criths, or 2.8672 grms. and by dividing the total weight of sulphurous anhydride obtained, viz., 20 grms. by the weight of one litre of the gas, we have—

$$\frac{20}{2.8672} = 6.975 \text{ litres of SO}_2.$$

8. How much chlorine gas by weight, and by volume, can be obtained by the action of excess of hydrochloric acid on 16 grms. of black manganic oxide, MnO<sub>2</sub>?

$$87 : 71 :: 16 : x.$$

Molecular      The weight of  
weight of      a molecule  
MnO<sub>2</sub>.      of chlorine.

*Ans.* 13.057 grms. of Cl.

Now one litre of chlorine weighs 35.5 criths, or  $\cdot 0896 \times 35.5 = 3.1808$  grms.

$$\frac{13.057}{3.1808} = 4.104 \text{ litres of chlorine gas.}$$

9. When carbon is burnt in oxygen gas it forms carbonic anhydride gas  $\text{CO}_2$ . How much carbonic anhydride by weight, and by volume, can be obtained by thus burning 15 grms. of carbon?

$$\begin{array}{ccccccc} 12 & : & 44 & :: & 15 & : & x. \\ \text{Atomic} & & \text{Molecular} & & & & \\ \text{weight of C.} & & \text{weight of CO}_2. & & & & \end{array}$$

*Ans.* 55 grms. of  $\text{CO}_2$ .

One litre of carbonic anhydride gas weighs 22 criths, or  $\cdot 0896 \times 22 = 1.9712$  grm.

$$\text{and } \frac{55}{1.9712} = 27.90 \text{ litres of carbonic anhydride gas.}$$

10. How much hydrogen and oxygen by weight and by volume can be obtained, by electrolysis, from 10 grms. of water?

$$\begin{array}{ccccccc} 18 & : & 2 & :: & 10 & : & x. \\ \text{Molecular} & & \text{Weight of} & & & & \\ \text{weight of OH}_2. & & \text{mol. of hydrogen.} & & & & \end{array}$$

*Ans.* 1.111 grms. of H.  
8.889 grms. of O.

One litre of H weighs  $\cdot 0896$  grm., hence—

$$\frac{1.111}{\cdot 0896} = 12.4 \text{ litres of hydrogen gas.}$$

One litre of oxygen weighs 16 times as much as one litre of hydrogen gas, *i.e.*,  $\cdot 0896 \times 16 = 1.4336$  grm.

$$\frac{8.889}{1.4336} = 6.200 \text{ litres of oxygen gas.}$$

11. You have given to you five litres of chlorine gas: how much metallic sodium is required to convert the whole of the chlorine into sodic chloride?

*Ans.* 10.304 grms. of Na.

12. 15 grms. of ferrous sulphide are treated with dilute hydrochloric acid: how much  $\text{SH}_2$  by weight, and by volume, can be obtained theoretically therefrom?

*Ans.* 5.795 grms. by weight, and 3.804 litres of  $\text{SH}_2$ .

## CHAPTER XI.

## ATOMICITY OR QUANTIVALENCE OF ATOMS.

ACCORDING to the law of multiple proportions, atoms can combine with atoms in more than one proportion, *i.e.*, one atom with two, three, four, or more other atoms.

Some few metals and metalloids can form only one oxide, sulphide, chloride, others two or more. Thus we have seen that binary compounds, such as:—

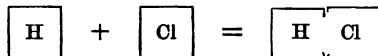
FeO.	FeS.	FeCl <sub>2</sub> .
MgO.	MgS.	MgCl <sub>2</sub> .
CuO.	CuS.	CuCl <sub>2</sub> .
ZnO.	ZnS.	ZnCl <sub>2</sub> .

are comparatively simple bodies. In fact, the number of atoms in the higher binary compounds of mineral or inorganic origin can mostly be expressed by the multiples 3, 4, 5.

We have seen (page 64) that under the continued influence of sunlight, chlorine water is decomposed into hydrochloric acid, which is absorbed by the water, and oxygen; and that for every two volumes of chlorine gas, when placed over water, one volume of oxygen will be found after some time. Two atoms of chlorine exert, therefore, the same combining power as one atom of oxygen.

Experiment 62 has also shown that sulphur is displaced by chlorine in sulphuretted hydrogen with formation of hydrochloric acid gas without any change in the respective volume composition.

Experiment 2 has demonstrated that the action of dilute hydrochloric acid on zinc liberated hydrogen, whilst the chlorine remained combined with the metal zinc, forming zincic chloride. We have since seen that hydrogen and chlorine in hydrochloric acid gas are combined in equal volumes:—



consequently we know that for every molecule  $\boxed{\text{H}} \boxed{\text{H}}$  of the liberated hydrogen gas two volumes (two atoms) of chlorine remain in combination with the metal zinc, and that therefore two molecules of hydrochloric acid must have taken part in the reaction—



Zincic chloride has the composition  $\text{ZnCl}_2$ ; one atom of zinc accordingly possesses the chemical combining power of two atoms of hydrogen, and two atoms of chlorine are of the same chemical



*combining value* as one atom of oxygen (comp. Exp. 63); they are in fact *equivalentic*. The same holds good for other metals, such as calcium, iron, manganese, copper, mercury, *i.e.*, they all unite with the same number of atoms of chlorine, *viz.*, two.

Experiment 1 has shown that the metal sodium decomposes water by taking the place of the hydrogen therein. Chlorine in Experiment 67 also combined directly with the metal forming common salt, NaCl, a compound which is in every respect analogous in constitution to hydrochloric acid, HCl. Sodic chloride can be readily prepared by the decomposition of this acid by means of sodium, hydrogen being evolved.

**Experiment 70.**—In order to illustrate this, collect by displacement some dry hydrochloric acid in a cylinder, by heating concentrated hydrochloric acid in a flask (Fig. 53) and passing

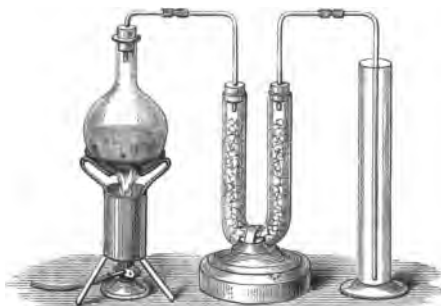


FIG. 53.—COLLECTING DRY HYDROCHLORIC ACID GAS BY DISPLACEMENT.

the gaseous acid which comes off through a U-tube filled with pumice-stone, moistened with oil of vitriol. The gas being heavier than air, may be collected in dry cylinders by passing the delivery tube down to the bottom of the cylinders, loosely covered with a piece of card-board, or better still, over mercury. On introducing a small piece of ignited sodium, placed in a deflagrating spoon into a cylinder full of hydrochloric acid gas, the sodium which at first burns at the expense of the oxygen of the air continues to burn in the hydro-

chloric acid gas at the expense of the chlorine, *i.e.*, it combines with the chlorine, setting free the hydrogen, and forms sodic chloride—



FIG. 54.—DECOMPOSITION OF HCl BY SODIUM

**Experiment 71.**—It may also be shown analytically, according to Hofmann, by filling a U-shaped bent tube (Fig. 54), open at one end with mercury, so as to displace all the air. By opening the compression clamp, the mercury is almost entirely run off from the open limb of the U-tube into a receiving vessel. Dry hydrochloric acid gas evolved as described in the previous experiment, is now introduced into the closed limb, which remained filled with the mercury, by means of a narrow delivery tube, provided with a piece of flexible india-rubber tubing, so as to be readily passed round the bend into the closed limb of the U-tube. Whilst this latter is charged to about two-thirds full with the dry gas, the mercury is allowed to run off from the little branch tube, provided with a compression clamp. Withdraw now the delivery tube, and equalise the level of the mercury in both limbs before tightening the compression clamp. Adjust the

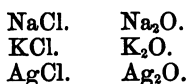
india-rubber ring, so as to mark the height of the mercury in the closed limb, and by means of another india-rubber ring, mark the line which divides the gas into two halves. Fill the open limb with sodium amalgam.\* Close the tube with the thumb and transfer the gas into the limb containing the amalgam, and agitate it briskly. The sodium abstracts the chlorine from the  $\text{HCl}$ , forming with it sodic chloride, and leaves hydrogen. Transfer the latter back again into the closed limb, and remove the thumb. Equalise the level of the mercury once more in both limbs by opening the tap. It will now be found that the gas fills only half the space which it originally occupied, and that the mercury has ascended to the upper india-rubber ring. Fill the open limb again with mercury, close with the thumb, and retransfer the gas which is left to the open limb. On withdrawing the thumb and applying a light to the gas, it will be found to burn with a bluish flame where it is in contact with the air. It is in fact hydrogen gas, for neither chlorine nor hydrochloric acid gas is a combustible gas.

This proves that two volumes of dry hydrochloric acid gas (or a molecular volume) contain equal volumes of hydrogen and chlorine. The metal sodium by combining with the chlorine, left the hydrogen in the free state.

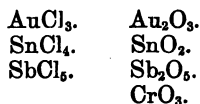
One atom of sodium possesses the same chemical displacing power as one atom of hydrogen, and two atoms of sodium must be required to combine with one atom of oxygen (in the same manner as two atoms of hydrogen were required to combine with one atom of oxygen in water), and the formula of the resulting sodic oxide must therefore be written—



The same holds good for several other metals, viz., potassium, silver; and the respective formulæ of the chlorides and oxides of these metals are therefore—



Other metals† again combine with 3, 4, 5, or 6 atoms of chlorine, or  $1\frac{1}{2}$ , 2,  $2\frac{1}{2}$ , and 3 of oxygen; such as the metals gold, tin, antimony, chromium. Their respective oxides and chlorides are thus written—



$\text{AuO}_4$  and  $\text{SbO}_3$  being inadmissible for reasons already stated.

Sulphur forms with metals compounds almost precisely analogous to those which oxygen forms.

In order to mark the binding capacity or atom-fixing power, [called *atomicity* or *quantivalence*] of the various elements, six divi-

\* Prepared by gradually dissolving about 10 pieces of sodium the size of a pea, in 50 c.c. of mercury.

† The tables showing the most important oxides, sulphides, and chlorides, will furnish further illustrations of the combining capacities of the different metals.

sions have been adopted by chemists, of which the following metals may be regarded as the representatives:—

Na, Mg, Au, Sn, Sb, Cr.

An element which combines with 1 atom of chlorine is *monovalent* or *monadic*; other elements which combine with 2, 3, 4, and 5 atoms of chlorine (or in the place of 6 of chlorine with 3 of oxygen), are *di-*, *tri-*, *tetra-*, *penta-*, and *hexa-valent* (from *valere*—to be of value), shortly called *monads*, *dyads*, *triads*, *tetrads*, *pentads*, and *hexads*. Elements with an odd number of bonds are called by Dr. Odling *perissads* (from *περισσός*, uneven, odd); whilst those with an even number are termed *artiads* (from *ἄριος*, even).

Oxygen, we have seen, is combined in water with two atoms of hydrogen: it is therefore divalent, or one atom of oxygen is equivalent to two atoms of hydrogen. Sulphur in sulphuretted hydrogen is divalent; and one atom of sulphur is equivalent to two atoms of hydrogen.

Boron combines with three atoms of chlorine to form boric chloride,  $\text{BCl}_3$ . Carbon combines with four atoms of hydrogen to form marsh-gas,  $\text{CH}_4$ , one of the constituents of coal gas. Pentavalent elements are the elements constituting the nitrogen group, N, P, As, and Sb.

Hydrogen is thus called upon to perform fresh functions, for it forms also the *unit of the binding or atom-fixing as well as atom-displacing power* inherent in every elementary body, as it already constituted the unit of atomic and volume combination. This atom-fixing power of elements is well illustrated whenever elements combine directly with hydrogen; as when oxygen attracts to itself two, nitrogen three, or carbon four, atoms of hydrogen.

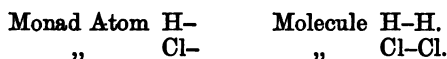
It must not be supposed that in the absence of metallic compounds with hydrogen, the combining capacity of metals (and non-metals) for chlorine—the equivalent for hydrogen—has been the only criterion for determining the atomicity or quantivalence of the different elements. Comparatively modern discoveries in the chemistry of *organic* bodies, in which metals are combined with a certain number of atoms of the organic analogues of hydrogen, methyl, ethyl, etc., have but recently introduced this method of determination. The coefficients of atomicity are, moreover, not yet determined experimentally for all metals, and we have in many cases to assume them by reasoning from analogy only. But whilst the atomicity of many elements must still be considered as provisional, and open to revision, yet the system of classification founded upon atom-fixing power has so much simplified the study of chemistry, that its introduction, even in its present incomplete state, into text books, cannot fail to recommend itself strongly to the student, as it supplies him with a generalisation which greatly facilitates the comprehension of chemical phenomena. Moreover, the doctrine of atomicity is in strict harmony with the atomic hypothesis.

We connect, then, with atoms not merely the notion of indivisibility and a definite relative atom- and volume-weight, but likewise

varying degrees of inherent affinity and a capacity of fixing or displacing a definite number of other atoms. Thus the atomic theory gains in importance as it gains in extent.

*Symbolic representation of the powers of Atoms in fixing or displacing other Atoms.*

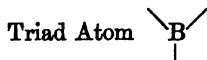
We represent to ourselves atoms as the smallest possible particles of matter, and in the absence of any experimental evidence as to their form may, for the sake of convenience, view them as spheres. We explain chemical combination between two elements as arising from the intimate union which takes place between their atoms, owing to the chemical affinity peculiar to each individual atom. If an atom exhibits an affinity by which its atom-fixing power becomes exhausted by combining with an atom of another element whose atom-fixing power equals that of hydrogen, taken as unit, it is manifestly a *monovalent* element or a monad,—it can bind or satisfy only one affinity. The atomicity of an element such as hydrogen or chlorine may be represented graphically, thus :—



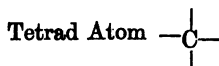
An atom of a element like magnesium, capable of fixing two monad atoms of chlorine, would then have to be represented graphically, thus :—



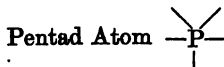
An element capable of fixing 3 atoms of chlorine, thus :—



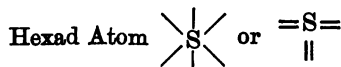
An element capable of fixing 4 atoms of hydrogen, thus :—



An element capable of fixing 5 atoms of chlorine, thus :—



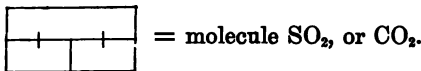
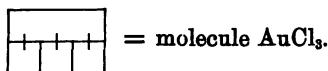
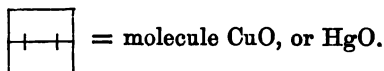
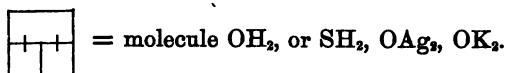
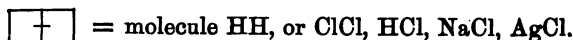
An element capable of fixing 3 atoms of the dyad oxygen, thus :—



Symbolic notation conveys the same idea if we employ dashes, and for the higher atomicities Roman figures placed to the right-hand side slightly above the symbols, thus :—

Hydrogen....	H' (written mostly without the dash).
Oxygen.....	O''
Boron .....	B'''
Carbon .....	C <sup>iv</sup>
Phosphorus ..	P <sup>v</sup>
Sulphur ....	S <sup>vi</sup>

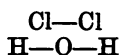
Other modes of graphic representation would answer equally well and have actually been used for this purpose, thus:—



This method of graphic representation possesses the advantage of setting forth in a marked manner the quantivalence of atoms as well as their molecular combining conditions. The second formula, *e.g.*, shows at a glance that two atoms of hydrogen are combined with one atom of oxygen, and that, therefore, the atom oxygen is equivalent to two atoms of hydrogen. Formula 5 shows in like manner that four atoms of hydrogen are combined with one atom of carbon, and hence that this latter element is equivalent to four atoms of hydrogen or chlorine.

At the same time this graphic representation is liable to mislead if the idea be entertained for a moment that an atom of carbon is four times, or an atom of oxygen twice as large as an atom of hydrogen or chlorine; and as no graphic representation whatever can claim to elucidate "*either the shape or size of an atom or molecule, nor the relative position of the constituent atoms of any chemical compound,*" it will suffice if we simply link together their symbols by short connecting lines, in order to indicate their atom-fixing capacity.

Thus we write:—



In the following table, taken from Dr. Frankland's "Lecture Notes," page 32, will be found the 36 most important elements, classified according to their atomicity or respective quantivalence. Metalloids are printed in *italics*. The different classes are again sub-divided into sections, representing elements closely resembling each other in their chemical character :—

Monads, or Monovalent Elements.	Dyads, or Divalent Elements.	Triads, or Trivalent Elements.	Tetrads, or Tetravalent Elements.	Pentads, or Pentavalent Elements.	Hexads, or Hexavalent Elements.
<i>1st Section.</i> <i>Hydrogen.</i>	<i>1st Section.</i> <i>Oxygen.</i>	<i>1st Section.</i> <i>Boron.</i>	<i>1st Section.</i> <i>Carbon.</i> <i>Silicon.</i> <i>Tin.</i>	<i>1st Section.</i> <i>Nitrogen.</i> <i>Phosphorus.</i> <i>Arsenic.</i> <i>Antimony.</i> <i>Bismuth.</i>	<i>1st Section.</i> <i>Sulphur.</i>
<i>2nd Section.</i> <i>Fluorine.</i> <i>Chlorine.</i> <i>Bromine.</i> <i>Iodine.</i>	<i>2nd Section.</i> Barium. Strontium. Calcium. Magnesium. Zinc.	<i>2nd Section.</i> Gold.	<i>2nd Section.</i> Aluminium.		<i>2nd Section.</i> Chromium. Manganese. Iron. Cobalt. Nickel.
<i>3rd Section.</i> Potassium. Sodium.	<i>3rd Section.</i> Cadmium. Mercury. Copper.		<i>3rd Section.</i> Platinum.		
<i>4th Section.</i> Silver.			<i>4th Section.</i> Lead.		

The elements have been classified according to their highest *atomicity* or greatest number of bonds. Thus sulphur *can* be made to combine with 3 atoms of the dyad element oxygen, although under ordinary conditions it combines only with 2 atoms of oxygen to form sulphurous anhydride gas,  $\text{SO}_2$ . In this instance the sulphur acts the part of a tetrad. Again, sulphur combines with two atoms of hydrogen, and is then for the time being a dyad element. The active atomicity or quantivalence of an element, therefore, principally depends on the nature of the elements with which it enters into combination. A hexad atom does not necessarily combine always with its maximum number of 6 chlorine atoms, or 3 atoms of oxygen, &c.; it may bind only four atoms of chlorine or 2 atoms of a dyad element, such as oxygen or sulphur; or 2 atoms of chlorine or its equivalent of a dyad atom: but a hexad atom will never be found to link itself to 5 or 3 or 1 atom of a monad element. *Its atomicity co-efficient is invariably an even number.* If the co-efficient be 2 or 4, instead of 6,—4 or 2 bonds respectively become, so to speak, *dormant* or *inactive*, and are indicated by dashes or Roman figures placed on the left-hand side, slightly above the symbols; but the *absolute* atom-fixing power of the hexad remains the same, and the dormant, or *latent* bonds, as Dr. Frankland calls them, may be called into activity by fresh chemical agencies,

whenever it is desired. The sum of the active and latent bonds must evidently always be equal to the absolute atomicity of an element.

Then, again, a pentad atom need not necessarily combine with 5 atoms of chlorine, &c. It may exist in combination with 3 atoms, or 1 atom, but never with 4 or 2 atoms of chlorine, or its equivalent. *Its atomicity co-efficient is invariably an uneven number.*

Elements which in the above list are classified as *monads*, &c., may possibly be discovered to be capable of a higher binding power. Compounds may exist, or may yet be discovered, in which the monad element exists as a triad or pentad, or the tetrad or hexad element as a hexad or octad; but it may safely be predicted that a monad element will never bind 2 atoms of chlorine, but only 3 or 5, and that its atomicity co-efficient will be found to be an uneven number, and that of a dyad always an even one.

*Use of Thick Type.*—The formulæ of the different chemical compounds are, according to Dr. Frankland's system, written in such a manner as to denote "that the element represented by the first symbol of a formula, is directly united with all the active bonds of the other elements or compound radicals following upon the same line." Thus the formula of water,  $\text{OH}_2$ , signifies that the dyad atom of oxygen is combined with the two bonds of the two atoms of hydrogen. The formula of carbonic anhydride,  $\text{CO}_2$ , signifies that the tetrad atom of carbon is combined with the four bonds of the two atoms of dyad oxygen. The first symbol constitutes the *grouping* element, and whenever this element has more than one bond, it will always be printed in thick type. The element having the greatest number of bonds will, as a rule, occupy this prominent position.

#### QUESTIONS AND EXERCISES.

1. How would you demonstrate analytically that hydrochloric acid consists of equal volumes of hydrogen and chlorine?
2. Give reasons why two molecules of hydrochloric acid ( $\text{HCl}$ ) are required to act upon an atom of zinc.
3. How would you demonstrate synthetically that hydrochloric acid gas is composed of equal volumes of  $\text{H}$  and  $\text{Cl}$ ?
4. Assign reasons for the formulæ  $\text{NaCl}$  and  $\text{ONa}_2$ .
5. Classify the following elements according to their respective atom-fixing power:— $\text{Br}$ ,  $\text{B}$ ,  $\text{C}$ ,  $\text{N}$ ,  $\text{Sn}$ ,  $\text{S}$ ,  $\text{Mg}$ ,  $\text{Ag}$ ,  $\text{Cd}$ ,  $\text{Pt}$ ,  $\text{Si}$ ,  $\text{As}$ ,  $\text{Mn}$ .
6. Commit to memory the 36 most important elements as classified in the preceding table.
7. Explain the terms *perissads* and *artiads*.
8. How can the atomicity of elements be indicated, 1st symbolically, 2nd graphically?
9. Explain what you understand by *absolute atomicity*, *active* and *latent bonds*, *grouping elements*.
10. State how many atoms of the following elements  $\text{Cl}$ ,  $\text{O}$ ,  $\text{S}$ , you consider equivalent to an atom of copper, of silver, or of antimony, platinum, gold, iron.
11. Represent graphically a molecular volume of  $\text{HCl}$ ,  $\text{OH}_2$ ,  $\text{BCl}_3$ ,  $\text{CH}_4$ , so as to indicate the atomicity of the respective elements, and state what objections can be urged against such graphic representation.
12. Place the atomicity co-efficient against the following elements:— $\text{P}$ ,  $\text{Hg}$ ,  $\text{Sr}$ ,  $\text{F}$ ,  $\text{I}$ ,  $\text{Cr}$ ,  $\text{Au}$ .
13. Place atomicity co-efficients against the elements constituting the oxides, sulphides, and chlorides enumerated in the tables on pages 50, 60, and 70.

## CHAPTER XII.

**HYDRATES—METALLIC AND NON-METALLIC.—  
PEROXIDES, HYDROXYL. FORMATION OF  
ACIDS FROM ANHYDRIDES. REACTIONS IN  
THE WET WAY. COMPOUND RADICALS.**

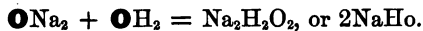
IN most of the reactions hitherto described we have restricted ourselves to changes which take place in the *dry* way, between solid bodies. In the few instances in which a liquid body reacted upon a solid body—as in the case where metallic sulphides were formed by the combination of a metal with the liquid sulphur, or where a liquid metal, such as mercury, or a readily fusible metal, like sodium, combined with oxygen or chlorine—one of the reacting bodies was rendered liquid by the application of heat. Such changes are called *reactions in the dry way*.

There are, however, a vast number of reactions, where the presence of water forms an essential feature, either by virtue of its solvent action (whereby substances are brought into more intimate contact), or by giving up a part or the whole of its constituent elements for the formation of the molecules of the new body. Such changes are termed *reactions in the wet way*.

Certain bodies, as soda, eagerly attract to themselves the moisture contained in our atmosphere. There can be no doubt that a *chemical* combination takes place between these bodies and the water, accompanied by the liberation of much heat. This is proved, moreover, by the difficulty with which soda gives up its water again when heated.

**Experiment 72.**—Evaporate a little solution of caustic soda in a small iron basin, or, better still, in a silver crucible or evaporating dish. It loses water, and acquires a syrupy consistency. On cooling, the mass solidifies.

Quantitative experiments have shown that one molecule of water is retained by the fused mass for every molecule of soda,  $\bullet\text{Na}_2$ . Dry soda, such as is formed by the oxidation of the metal sodium in a current of dry oxygen gas, combines with 1 molecule of water, and the change may be viewed as an addition of two binary compounds according to the equation—



The new *ternary* body contains the elements of soda and water truly chemically combined. In fact, soda acquires its characteristic caustic nature only by this very act of combination with water— $\bullet\text{Na}_2$  is without action upon dry litmus-paper.

**Experiment 73.**—Heat some finely granulated zinc or zinc turnings and a strong solution of sodic or potassic hydrate in a small flask provided with a gas delivery tube, and collect the gas which is slowly evolved over water. As



soon as a sufficient amount of gas has been collected, remove the test-tube from the pneumatic trough, and apply a lighted taper. The gas burns at the mouth of the tube with the characteristic lambent flame of hydrogen.

This shows that concentrated hydrated alkali is decomposed by the metal zinc with formation of potassic zincic oxide and evolution of hydrogen, thus:—



The new body constitutes a quasi saline compound, in which the strong alkali acts the part of the base and the zincic oxide that of a weak acid. This may be shown by adding sulphuretted hydrogen water to the solution, when a white precipitate of zincic sulphide, **ZnS**, comes down. The metals aluminium, cadmium, and magnesium give rise to reactions of a similar nature. They dissolve even in the cold when placed in contact with platinum, iron, etc., in alkaline solutions with evolution of hydrogen.

**Experiment 74.**—A little burnt lime, **CaO** (quicklime) is placed in a porcelain dish, and moistened with as much water as it will take up within its pores. The mass soon begins to get hot; it gives off steam, and falls to pieces.

Much heat is evolved by the chemical combination of lime with water. Quantitative experiments have proved that this reaction takes place according to the equation—



Numerous metallic oxides are met with in nature, both in the anhydrous and hydrated condition, *e.g.*, the oxides of iron, manganese, aluminium, copper (comp. Table, p. 50); some combine with more than one molecule of water, and form more than one hydrate. Some hold the water with various degrees of force; cupric hydrate, **CuHo**<sub>2</sub>, parts with its water at a very moderate heat, calcic hydrate at a very strong red heat, whilst potassic or sodic hydrate are not decomposed by the strongest heat which can be applied to them. A few only are readily soluble in water, and deserve our special attention, *viz.*, the hydrates of potassium, sodium, barium; others are moderately soluble, *e.g.*, strontic and calcic hydrate. All these form strongly alkaline solutions. Others, again, are insoluble, or nearly so, *e.g.*, magnesian hydrate, plumbic, mercuric, and argentic hydrate.

**Experiment 75.**—Heat some plumbic oxide (*Massicot*), **PbO**, for several hours in a small porcelain dish or iron spoon below the point where it fuses (below 300° C.). Stir occasionally with a glass or iron rod. The bright yellow oxide absorbs slowly oxygen from the air, and is converted into a fine red powder, called red lead or minium, consisting of varying quantities of lead and oxygen, usually of the formula **Pb<sub>3</sub>O<sub>4</sub>**. This is generally done on a manufacturing scale by heating plumbic oxide in a reverberatory furnace with constant stirring. That oxygen has been taken up may be readily proved by heating some red lead in a tube (Fig. 55), when oxygen is given off again, and the yellow oxide is left, thus:—**Pb<sub>3</sub>O<sub>4</sub>** = 3**PbO** + **O**.

On account of the facility with which the red lead parts with a fourth of its oxygen, it is used as an oxidising agent in making

flint glass, the plumbic oxide combining at the same time with the white sand or silica.

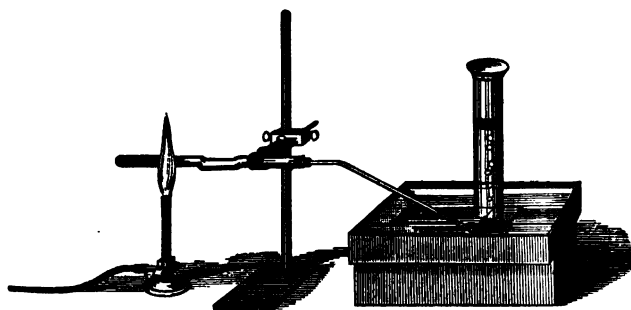


FIG. 55.

**Experiment 76.**—Treat some red lead with dilute nitric acid, and heat gently for some time in a porcelain dish. The brilliant red colour changes to a deep brown, owing to the acid dissolving out two parts of  $PbO$ , with which it forms a salt called plumbic nitrate, and leaving plumbic dioxide,  $PbO_2$ . This, when filtered off, washed, and dried at a gentle heat, constitutes a dark purplish brown coloured body, which yields half its oxygen upon the application of a gentle heat, and is reduced to the yellow plumbic oxide.

**Experiment 77.**—Pass dry air or oxygen over lumps of baric oxide,  $BaO$ , heated in a porcelain tube to from  $300^{\circ}$  to  $400^{\circ}$  C. The baric oxide takes up oxygen, without altering its form, changing merely from white to a greyish colour, and forms a peroxide,  $BaO_2$ , containing double the amount of oxygen. On heating this per- or dioxide (also called binoxide or hyperoxide) to full redness, it loses its second atom of oxygen again, and becomes reconverted into baric oxide. On treating it with a little water it forms a white hydrate, which is little soluble in water, and which gives off oxygen on boiling, and is converted into baric hydrate,  $BaO_2H_2$ , or  $BaHO_2$ , which dissolves readily in water.

It has been proposed to utilize this property of baric oxide of combining with oxygen at a low heat, and giving it up again at a high heat, for the wholesale manufacture of oxygen gas.

This body possesses, however, additional interest, as it forms the usual starting point for the preparation of peroxide of hydrogen, or hydric peroxide,  $O_2H_2$ .

**Experiment 78.**—Suspend some finely divided baric peroxide in water, and pass a current of carbonic anhydride. The hydrated baric peroxide breaks up into hydric peroxide and baric oxide, which by combining with the carbonic anhydride forms insoluble baric carbonate, which can be filtered off from the soluble hydric peroxide. The solution should be concentrated by slow evaporation, by placing it under a bell-jar in a porcelain dish over oil of vitriol.

Hydric peroxide,\* also called *hydroxyl* (molecule), forms a colourless liquid of syrupy consistency, and possessing a peculiar odour. Its specific gravity is 1.452. It does not solidify at

\* A solution of hydric peroxide containing a little free acid (hydrochloric or sulphuric), is now sold for medicinal and photographic purposes, also as a hair-wash, for it bleaches the hair, and produces a much admired golden yellow colour.

— 30° C. It is very unstable, and begins to decompose spontaneously at 15° to 20° C., more rapidly so when heated—sometimes with explosive violence. Dilute solutions of hydric peroxide, especially if they contain a little hydrochloric or sulphuric acid, are more permanent.

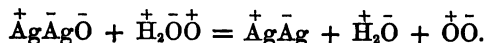
**Experiment 79.**—Nearly fill a small flask, fitted with a narrow delivery-tube, with hydric peroxide. Add a drop of sodic hydrate, and heat gently in a water-bath till the evolution of oxygen begins. Collect the gas over water, and ascertain by the usual tests that it is oxygen.

This experiment shows that heat breaks up hydric peroxide into water and oxygen, analogous to the change which plumbic dioxide and baric peroxide underwent when heated, only far more readily. On this account hydric peroxide constitutes one of the most powerful oxidizing agents with which we are acquainted. The second atom of oxygen separates from hydroxyl under various and often enigmatical circumstances in the form of gas, the volume of which amounts to 475 times that of the liquid. Great heat is also developed, and when the experiment is made in the dark even light is apparent.

Certain bodies, among which are charcoal, many metals, and some metallic oxides, induce by their mere contact a more or less violent decomposition of the peroxide into  $\text{H}_2$  and O, *without themselves undergoing any change*; gold, platinum, and silver, particularly when in the precipitated or spongy state, act most violently, and cause a great disengagement of heat. This chemical decomposition by mere contact is termed *catalytic* action; its nature, however, is not at present understood.

**Experiment 80.**—Allow a drop of hydric peroxide to fall upon brown argentic oxide. Decomposition takes place with explosive violence and great evolution of heat. The silver oxide loses its oxygen, and is reduced to grey metallic silver.

The oxides of gold, platinum, or mercury are acted upon in a similar manner, likewise the peroxides of lead and manganese, as well as several other more highly oxidized bodies. The explanation for this interesting reaction, first minutely examined and explained by Sir B. Brodie, is that the second atom of oxygen in the peroxides of hydrogen and barium is not merely retained in an unstable state of combination, but that it is, by association with the oxide of an electropositive element like hydrogen or barium, thrown into a polar state, opposite to the polar state of the oxygen in unstable protoxides, and to that of the loosely combined oxygen in the more or less electropositive (chlorous) peroxides. Hence the two oppositely polarized oxygen atoms unite with one another, as indicated in the following equation:—



Hydric peroxide, which in the last experiment acted as a most powerful reducing agent, is frequently employed for purposes of oxidation.

**Experiment 81.**—Soak some filter paper in a solution of plumbic acetate (sugar of lead), and expose the paper to sulphuretted hydrogen gas. Black plumbic sulphide (**PbS**) is formed. Wash and dry the paper, then brush it over with a solution of hydric peroxide. The black plumbic sulphide is instantaneously oxidized and converted into plumbic sulphate. Old oil paintings discoloured by the formation of plumbic sulphide, may be cleansed by washing with a dilute solution of hydric peroxide.

Certain metallic hydrates are readily peroxidized by exposure to the atmosphere, more especially in the presence of an alkali (soda, lime, etc., etc.).

**Experiment 82.**—Dissolve some manganous chloride, **MnCl<sub>2</sub>**, in water, and add a solution of sodic hydrate as long as a precipitation takes place. Filter and wash with a little hot water; then take some of the flesh-coloured manganous hydrate, **MnO<sub>2</sub>H<sub>2</sub>**, or **MnHCO<sub>3</sub>**, off the filter by means of a glass spatula, and spread it out in a thin layer on a porcelain slab or plate. The hydrate becomes rapidly brownish black, owing to the absorption of atmospheric oxygen, with which the manganous oxide forms a more highly oxidized body, of the composition **Mn<sub>2</sub>O<sub>3</sub>.OH<sub>2</sub>**, or  $\begin{cases} \text{MnOH} \cdot \text{O} \\ \text{MnOH} \cdot \text{O} \end{cases}$ .

This affinity for oxygen observed long ago by chemists, in the lower oxide of manganese, has been practically utilized of late for recovering the manganese from the chlorliquo, formerly run to waste by the manufacturers of bleaching powder. The oxidation is effected by blowing air through a mixture of milk of lime and manganous hydrate.

The lower hydrated oxides of iron and of cobalt are acted upon in a similar manner by atmospheric oxygen, in the presence of an alkali (ammonia, soda).

The oxides of non-metallic elements, such as of phosphorus or sulphur, exhibit the same affinity for water as some of the metallic oxides.

Phosphoric anhydride, **P<sub>2</sub>O<sub>5</sub>**, absorbs moisture with great avidity from the atmosphere. A few flakes of the anhydride, when thrown into water, cause a hissing noise, and dissolve instantaneously, giving rise to an increase of temperature.

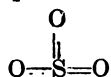
**Experiment 83.**—Sulphuric anhydride, **SO<sub>3</sub>**, is obtained as a white mass of crystals, resembling asbestos. When exposed to moist air the crystals fume, and rapidly deliquesce from absorption of aqueous vapour, and become converted into the hydrate, usually called sulphuric acid. Small portions of the anhydride when cautiously thrown into water, occasion each time a hissing sound, and the water gets intensely hot.

The heat must have been stored up in the anhydride and in the water (both cold bodies at the ordinary temperature).

The liquid reddens blue litmus-paper most intensely. On distilling the dilute acid in a retort, through the tubulure of which a thermometer is fitted air-tight by means of a soft cork, it yields first water, then hydrated acid, and the boiling-point rises gradually until it remains constant at 326° C. No further change is observed, and the remaining liquid rapidly distils over.

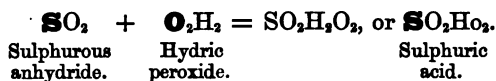
Quantitative experiments have proved that this distillate is a ternary compound of S, O, and H, viz., **SO<sub>4</sub>H<sub>2</sub>**, or **SO<sub>3</sub>.OH<sub>2</sub>**.

The compound **S<sup>VI</sup>O<sub>3</sub>** is represented graphically :—

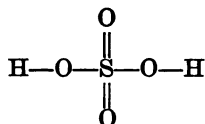


On passing sulphurous anhydride\* slowly over plumbic dioxide,  $\text{PbO}_2$ , loosely spread out in a thin layer in a narrow tube of hard glass, the gas is eagerly absorbed by the binary compound, plumbic dioxide, with which it forms a white compound, called plumbic sulphate,  $\text{SO}_3\text{PbO}_2$ . The same reaction takes place when manganic oxide,  $\text{MnO}_2$ , is employed—manganous sulphate,  $\text{SO}_3\text{MnO}_2$ , being formed.

**Experiment 84.**—Add to a concentrated solution of sulphurous anhydride gas in water, a solution of peroxide of hydrogen,  $\text{O}_2\text{H}_2$ , until the odour of the sulphurous anhydride gas has entirely disappeared. Sulphurous acid is instantaneously converted into sulphuric acid on coming in contact with hydric peroxide.



If we then regard the chemical compound which is formed when  $\text{SO}_2$  and  $\text{O}_2\text{H}_2$  are brought together, as consisting of sulphurous anhydride gas and hydric peroxide, we shall be able to represent it graphically as follows:—



and preserve in this manner the hexad nature of the sulphur atom. Manganous sulphate, containing in the place of the two atoms of hydrogen a dyad element, Mn, and plumbic sulphate, the dyad element, Pb, would then be written graphically—

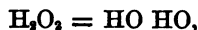


The compound  $\text{SO}_2$  is called sulphurous *anhydride* (from *an*, not, without, and *hidrōs*, water), and the compound  $\text{SO}_3$ , sulphuric anhydride; for oxides which form *acids* when they combine with water, or salts when added to bases, are termed *anhydrides*.

Water is usually viewed as an oxide of hydrogen. It may, however, also be regarded as a hydride of the semi-molecule HO. Many bodies of analogous nature occur among organic compounds, and we are, therefore, perfectly justified in taking this view of water, viz.:—



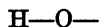
Hydric peroxide being then represented by—



\* The preparation of this gas will be fully described in Chapter XIV.

the compound  $\text{H}_2\text{O}_2$  consisting of two parts of the binary compound  $\text{HO}$ , which has not as yet been obtained in an isolated condition, but exists merely in the form of the molecule. One of the semi-molecules,  $\text{HO}$ , in  $\text{H}_2\text{O}_2$ , takes the place of  $\text{H}$  in  $\text{OH}_2$ , and it is, therefore, equivalent to  $\text{H}$ ; *i.e.*, it possesses the same binding power as hydrogen, or chlorine, or any other monad element. Such a group of elements which is capable of taking the place of one or more atoms of  $\text{H}$  is termed a *compound radical*. The radical  $\text{HO}$  has received the name of *hydroxyl*, and is conveniently expressed symbolically with a small  $\text{o}$  after the  $\text{H}$ , viz.,  $\text{Ho}$ ; it must not be supposed, however, for a moment that a different atomic value appertains to the small  $\text{o}$  than the large  $\text{O}$ . Hydric peroxide consists of two parts of the compound radical hydroxyl. Although  $\text{Ho}$  is a compound, it yet acts the part of a simple atom, because it enters into combination with other atoms, according to definite weight.

Graphic representation illustrates clearly its monad nature, for we must write hydroxyl—



only one hypothetical point of attachment of the oxygen atom being left by which it can join itself to hydrogen to form water, or to another hydroxyl radical to form hydric peroxide.

In like manner there must be as many compound radicals possible as there are metals. A few may be said to correspond to the peroxides, but in most cases they are purely hypothetical creations, as the peroxides of many metals are unknown; thus we have—

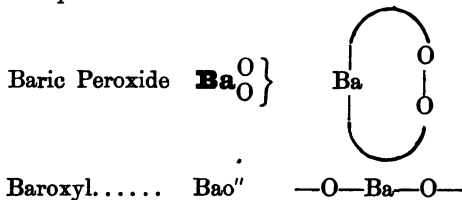
Metals.		Oxides.	Peroxides.	Compound radicals* corresponding to hydroxyl or its multiple.
Potassium.	$\text{K}$	$\text{OK}_2$	$\text{K}_2\text{O}_2 = \begin{Bmatrix} \text{OK} \\ \text{OK} \end{Bmatrix}$	$\text{Ko}$ (Potassoxyl).
Barium...	$\text{Ba}''$	$\text{BaO}$	$\text{BaO}_2 = \begin{Bmatrix} \text{O} \\ \text{O} \end{Bmatrix} \text{Ba}$	$\text{Bao}''$ (Baroxyl).
Magnesium	$\text{Mg}''$	$\text{MgO}$	—	$\text{Mgo}''$ (Magnesoxyl).
Zinc.....	$\text{Zn}''$	$\text{ZnO}$	—	$\text{Zno}''$ (Zincoxyl).
Iron.....	$\text{Fe}''$	$\text{FeO}$	—	$\text{Feo}''$ (Ferrosoxyl).
Lead.....	$\text{Pb}''$	$\text{PbO}$	$\text{Pb}^{\text{iv}}\text{O}_2$	$\text{Pbo}''$ (Plumboxyl).
Antimony.	$\text{Sb}'''$	$\text{Sb}_2\text{O}_3$	—	$\text{Sbo}'''$ (Antimonoxyl).
Bismuth..	$\text{Bi}'''$	$\text{Bi}_2\text{O}_3$	—	$\text{Bio}'''$ (Bismuthoxyl).

The atoms of oxygen in these compound radicals are represented by a small  $\text{o}$ , indicating their binding function, as distinct from the  $\text{O}$  atoms in the peroxides. In the peroxides the oxygen and metal

\* If it should be preferred to retain the large  $\text{O}$  for these compound radicals, they should be bracketed, and the atomicity coefficient placed outside the bracket, thus:—

$(\text{KO})$	Potassoxyl	$(\text{PbO}_2)''$	Plumboxyl
$(\text{BaO}_2)''$	Baroxyl	$(\text{SbO}_3)'''$	Antimonoxyl
$(\text{MgO}_2)''$	Magnesoxyl	$(\text{Al}_2\text{O}_3)^{\text{vi}}$	Aluminoxyl
$(\text{ZnO}_2)''$	Zincoxyl		

are connected by one bond only of the O atoms, whilst the remaining bonds of the oxygen atoms satisfy each other; this is indicated by bracketing the oxygen atoms. In the metalloxyds, on the other hand, the oxygen atoms are linked to one or more atoms of other elements, for example—



The dashes and Roman figures after the small o indicate that the compound radicals which these metals form, are capable of replacing one, two, three, etc., of the monovalent radical Ho.

On viewing in like manner the sulphuretted hydrogen gas,  $\text{SH}_2$ , which we obtained in Experiment 54, we may regard it either as water,  $\text{OH}_2$ , in which the oxygen atom has been replaced by an atom of sulphur, or as the hydride of a compound radical *hydrosulphyl*, HS, analogous to hydroxyl,—conveniently written with a small s, Hs, after the hydrogen, and represented graphically thus—

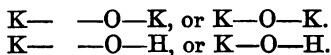


Only one point of attachment is left open in the dyad atom sulphur by which it can link itself to hydrogen to form sulphuretted hydrogen, or to a monad element, *e.g.*, sodium, Na, potassium, K, to form  $\text{NaHs}$ ,  $\text{KHs}$ .

The ternary chemical compounds which are obtained when water combines with metallic oxides to form *hydrates* must be expressed graphically in like manner. We may view potassic oxide,  $\text{OK}_2$ , as composed of the compound radical potassoxyl Ko—the radical in the molecule potassic dioxide ( $\begin{array}{c} \text{OK} \\ \text{OK} \end{array}$  or  $\text{K}_2\text{O}_2$ )—together with an atom of K, thus—



and potassic hydrate as a compound of K and Ho, the radical hydroxyl, Ho, replacing potassoxyl, Ko, in potassic oxide.



Metallic hydrates, then, may be viewed as binary compounds, in which one, two, three, or four parts of the compound radical hydroxyl are combined with one atom of a metal, according as the latter is of a monad, dyad, triad, or tetrad nature.

Hydrates of monad metals—  
 $\text{KHo} \cdot \text{NaHo} \cdot \text{AgHo}$

Graphically—  
 $\text{K}-\text{Ho}.$

Hydrates of dyad metals—



Hydrates of triad metals—

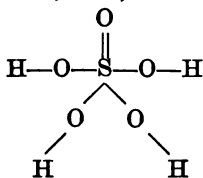


Hydrates of tetrad metals—

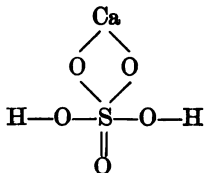


Some of the metallic oxides possess little or no affinity for water, or, if they combine with it, form only weak chemical compounds, which are broken up again on the application of heat, into water, which is given off, and oxides. On the other hand, metallic oxides are often capable of fixing more than one molecule of water; thus potassic hydrate (which is generally sold in the form of sticks, from having been run into cylindrical metallic moulds whilst in an oily condition; or in lumps, from being poured into flat iron vessels and broken up when cold), if left exposed to the air attracts moisture very rapidly, and forms an oily liquid—it *deliquesces*. Oil of vitriol, or sulphuric hydrate (which contains generally a little more than one molecule of water), also attracts moisture very eagerly. It is, therefore, employed for drying gases which are not acted upon by the acid. By passing gases through sulphuric hydrate, contained in a two-necked Woulfe's bottle, or through a drying tube filled with pumice-stone soaked in oil of vitriol, they are freed from moisture, and may be collected in a perfectly dry state. As the combination of a further molecule, or number of molecules of water with potassic hydrate or sulphuric hydrate is accompanied by a considerable rise in temperature, it is inferred that several hydrates of one and the same oxide may exist; and this is actually the case. A tetrahydric sulphuric acid, for instance, exists, which boils at  $242^\circ \text{C}$ ., and is formed from two molecules of water and one of sulphuric anhydride.

Symbol  $\text{SO}_3, 2\text{H}_2\text{O}$ , or  $\text{S}^{\text{O}}\text{Ho}_2\text{Ho}_2$ ,



A natural compound, called *gypsum* (dried at  $100^\circ \text{C}$ .), is the acid salt of this tetrahydric acid, viz.,  $\text{S}^{\text{O}}\text{Ho}_2\text{CaO}''$  (dihydric calcic sulphate).





It is usual to express dilute sulphuric acid by the formula  $\text{SO}_2\text{H}_2$ , and a solution of potassic hydrate or caustic potash, by the formula  $\text{KHO}$ , without regard to the amount of hydration which these bodies have undergone. The same formulæ, however, possess likewise a definite meaning, expressing, as has been already shown, in the strict sense of our symbolic notation, sulphuric monohydrate, potassic monohydrate.

#### QUESTIONS AND EXERCISES.

1. Define what is meant by reactions in the *wet* and *dry* way.
2. Give instances of combination between oxides and water, and state on what grounds you consider such compounds to be the result of a *chemical* and not merely mechanical combination.
3. Explain why hydrogen is evolved when zinc ( $\text{Al}$ ,  $\text{Cd}$ ,  $\text{Mg}$ ) is acted upon by a concentrated solution of potassic hydrate.
4. How is red lead manufactured from massicot?
5. How is red lead acted upon (1) by strong heat, (2) by nitric acid?
6. How is baric oxide converted into baric peroxide, and how would you prepare from the latter a solution of hydric peroxide?
7. Explain the action of heat upon a concentrated solution of hydric peroxide.
8. Mention instances of the oxidising action of hydric peroxide. Give equations.
9. Describe the action of air upon moist ferrous, manganous, or cobaltous hydrate.
10. What do we understand by the terms *ternary* compound, *anhydride*, *peroxide*, *hydroxyl*, *catalytic* action, *hydrosulphyl*, *deliquescence*?
11. Give symbolic and graphic formulæ of sulphurous and sulphuric anhydride, of dihydric sulphuric acid, of manganous sulphate, and of dihydric calcic sulphate.
12. Assign reasons for writing the symbolic formula of sulphuric acid,  $\text{SO}_2\text{H}_2$ , instead of  $\text{SO}_4\text{H}_2$ .
13. Define a *compound radical*. Give illustrations.
14. Write out the names of the compound radicals corresponding to hydroxyl, of the metals which are capable of forming the salifiable oxides enumerated on p. 50. Practise writing out symbolic and graphic formulæ thereof.
15. Give symbolic and graphic formulæ for baric peroxide, manganic oxide, plumbic dioxide, potassic dioxide, potassic hydrate, calcic hydrate, stannic hydrate, baroxyl, plumboxyl, argentic peroxide, argentoxyl, antimonious hydrate.
16. You have given to you quicklime, dilute sulphuric acid, and water; what chemical combinations are you able to produce with these materials?
17. Calculate the percentage composition of baric peroxide.
18. You have given to you 10 grms. of red lead and a solution of hydrochloric acid. State how you would prepare (1) oxygen, (2) chlorine, from these materials, and how much of each gas, by weight and by volume, you could prepare therefrom.

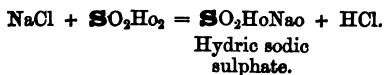
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#### CHAPTER XIII.

### HYDROCHLORIC ACID.—CONVERSION OF METALLIC OXIDES INTO CHLORIDES.

**Experiment 85.**—A flask fitted with a cork and delivery-tube is charged with a few pieces of fused sodic chloride; oil of vitriol is added in sufficient quantity to cover the salt. On gently heating, a colourless gas is evolved, which, on coming in contact with the air, fumes considerably.

The reaction is expressed by the equation—



Hydrochloric acid gas can be obtained perfectly anhydrous by passing it through a U-tube containing pieces of pumice-stone, moistened with oil of vitriol (as was shown in Fig. 53), and can then be collected by *displacement*. For this purpose pass the delivery-tube to the bottom of a perfectly dry globular flask. The lighter air is gradually lifted out of the flask (Fig. 56) by the heavier gas (the sp. gr. of HCl being 1.247, as compared with air), and its escape from the flask is marked by white fumes, produced by the combination of the otherwise transparent gas with the moisture of the air.

Hydrochloric acid gas possesses a powerful attraction for water.

In order to illustrate this, place the globular flask with its mouth downwards in a small capsule full of mercury. Transfer cautiously to a basin of water (Fig. 56), coloured blue by a few drops of litmus, and open the flask under water by raising its mouth out of the mercury. The water rushes in with great violence, for it is capable of absorbing 480 times its bulk of hydrochloric acid gas. The blue colour changes instantaneously to red.

**Experiment 86.**—Introduce a piece of freshly burnt lime (quick-lime) into dry hydrochloric acid gas, placed in a cylinder over mercury. The gas will be quickly absorbed and calcic chloride and water will be formed, according to the equation—



**Experiment 87.**—Introduce a lighted taper into a cylinder filled with dry hydrochloric acid gas. The taper is immediately extinguished.

Hydrochloric acid gas *does not support combustion*, nor is it combustible.

**Experiment 88.**—Pass a slow current of dry hydrochloric acid gas directly from the drying tube over freshly ignited cupric oxide,  $\text{CuO}$ , placed in a porcelain boat inside a tube of hard glass, in a manner similar to that shown in Fig. 22. The copper lays hold of the chlorine, and the oxygen combines with the hydrogen, according to the equation—



The water is carried along and partly condensed in the further part of the tube, or carried with the undecomposed hydrochloric acid into a bottle containing a solution of sodic hydrate. The black oxide of copper is converted into a greenish liquid, which is partly left in the boat, and partly volatilized and condensed with a portion of the water. The reaction takes place in the cold, but much more rapidly when the part of the tube containing the boat is gently heated. On allowing it to cool, and dissolving the cupric chloride left in the boat by the addition of a little water, a green solution is obtained.

The same change takes place when mercuric or zincic oxide is acted upon, according to the equation—

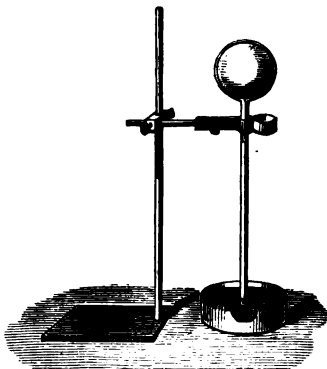
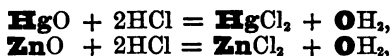


FIG. 56.—ABSORPTION OF HCl GAS BY WATER.



water being invariably produced, whilst metallic chlorides are formed. If no chloride exists corresponding to the oxide, part of the chlorine escapes, leaving a *lower* chloride of the metal as was the case in preparing chlorine from black oxide of manganese (Exp. 59), or when red lead is acted upon by hydrochloric acid.

A solution of hydrochloric acid gas in water (sometimes called spirit of salt, muriatic acid, from the word *muria*, brine, chlorhydric acid, and hydric chloride), is largely used in the laboratory, and constitutes one of the most indispensable reagents.

**Experiment 89.**—Put one part by weight of dry sodic chloride (common salt), and two parts by weight of concentrated sulphuric acid (previously diluted with one-third of water) in a flask (Fig. 47), shake well up, connect with two or three Woulfe's bottles, and apply a gentle heat. Small quantities of sulphuric acid, which may be carried over, are arrested in the first Woulfe's bottle. The delivery-tubes should be adjusted so as to dip barely into the water, because the hydrochloric acid is so eagerly absorbed by the water as to cause the contents of the Woulfe's bottles to recede, and because the acid liquid which is formed, being heavier than water, sinks rapidly to the bottom.

A solution of pure hydrochloric acid should be quite colourless.

**Experiment 90.**—Neutralize a solution of sodic hydrate, in the manner shown in Exp. 44, with dilute hydrochloric acid. The resulting sodic chloride, formed according to the equation—



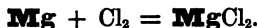
crystallises out on evaporation in a porcelain dish.

Pour off the liquid and spread the crystals on filter-paper, placed on a porous tile, to dry.

It follows from this experiment that a metallic chloride can be obtained also by neutralizing a solution of a metallic hydrate with dilute hydrochloric acid, and that such chlorides possess all the properties of chlorides obtained in the dry way.

Metallic chlorides can, with few exceptions, be prepared, as we have hitherto\* seen,

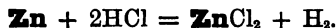
1. *By the direct combination of chlorine with metals* (comp. Expts. 65, 66, and 67), e.g.,



2. *By the action of hydrochloric acid, either in the gaseous form or as dilute acid, upon metals* (comp. Expts. 2 and 71), e.g.,



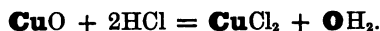
Gaseous.



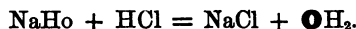
A dilute  
solution.

\* Other modes of forming metallic chlorides will be dealt with below.

3. *By the action of hydrochloric acid, no matter whether as gas or in solution, upon metallic oxides* (comp. Expts. 86 and 88), *or sulphides* (Exp. 54), *e.g.*,

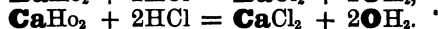
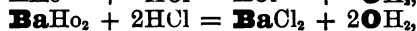
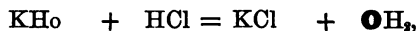


4. *By the action of dilute hydrochloric acid upon metallic hydrates* (comp. Exp. 90), *e.g.*,



Methods 3 and 4 of preparing chlorides, moreover, are the most convenient and most generally adopted, since metallic oxides or hydrates, which occur more frequently in nature than the metals, are much more easily and cheaply converted into chlorides than the metals themselves. This applies especially to the lighter metals, Na, K, Ba, Sr, Ca, Mg, Al.

We can prepare in this manner *potassic chloride, baric, and calcic chlorides*, etc., by neutralising their corresponding hydrates with dilute hydrochloric acid, according to the equations—

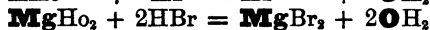
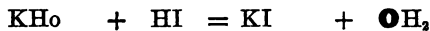


Solutions thus obtained are termed *chemical solutions*, because the solvent, HCl, forms with the dissolved substance a chemical compound.

It may be useful to examine for a moment somewhat more closely into the action of hydrochloric acid upon the more important metals (method 2), and to observe—

1. *That certain metals\* are readily dissolved with evolution of hydrogen, viz., K', Na', Ba'', Sr'', Ca'', Mg'', Al'', Fe'', Zn'', Cd'', Ni'', Co'', and (pulverulent) Cr''.*
2. *Others are only with difficulty soluble in boiling acid, viz., Sn''.*
3. *Others again are but slightly attacked by hydrochloric acid, viz., Sb''', Pb'', Ag', Bi''', Cu'', and*
4. *A few metals are not affected either by cold or hot hydrochloric acid, viz., Au, Pt, As, Hg, and (crystalline) Cr.*

Hydriodic, hydrobromic, and hydrofluoric acid act in a similar manner upon metallic hydrates. They form iodides, bromides, and fluorides, *e.g.*—



\* Practically no other but the few metals printed in thick type would ever be thus used for the preparation of metallic chlorides. The atomicity marks placed on the right hand side above the symbols indicate the nature of the chlorides which the different metals form under the given circumstances. Compare also table of metallic chlorides, p. 70.

All metallic iodides and bromides, with the exception of argentic iodide and bromide, are more or less soluble in water or dilute nitric acid. Metallic fluorides, on the other hand, are for the most part insoluble in water, with the exception of the alkaline and a few other fluorides. The best known fluoride is calcic fluoride, or *fluor spar*, insoluble in water and dilute acids.

#### QUESTIONS AND EXERCISES.

1. How would you demonstrate the great solubility of hydrochloric acid gas in water?
2. What is the action of dry HCl gas upon dry metallic oxides? Give equations.
3. How is a concentrated solution of hydrochloric acid prepared?
4. You have given to you a dilute solution of sodic hydrate and dilute hydrochloric acid: state how you would prepare from these materials crystals of common salt?
5. Explain the terms *neutralize*, *chemical solution*, *evaporation*.
6. Commit to memory the action of hydrochloric acid upon the more important metals.
7. Enumerate the different methods for preparing metallic chlorides, and state which methods you would follow if you had to prepare cupric chloride, mercuric chloride, zinc and ferrous chlorides, sodic chloride, stannous chloride. Give equations.
8. Give symbolic and graphic formulæ for antimonious, cupric, magnesian, cobaltous, manganous, and argentic chlorides.
9. How much sulphuric acid ( $\text{SO}_3\text{H}_2$ , molecular weight 98) is required to decompose 100 grms. of fused sodic chloride, so as to leave hydric sodic sulphate?
10. How much metallic zinc can be dissolved by 50 grms. of hydrochloric acid containing 20 per cent. of acid by weight?
11. How much dry hydrochloric acid gas by weight and by volume will be required to combine with 5 grms. of ignited cupric oxide?

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#### CHAPTER XIV.

#### FORMATION OF TERNARY OXY-COMPOUNDS FROM METALLIC HYDRATES AND OXY-ACIDS, SULPHUROUS AND SULPHURIC ACIDS, SUL- PHITES AND SULPHATES.

SULPHUR combines, as we have repeatedly seen, directly with oxygen, and forms a *binary* compound, *sulphurous anhydride*,  $\text{SO}_2$ , readily recognised by its pungent and suffocating odour. The gas is transparent and colourless, and does not burn nor support combustion (Exp. 22). It is soluble in water—1 volume of water dissolves at the ordinary temperature more than 40 volumes of the gas and furnishes by direct combination with it a *ternary* body, an acid, called *sulphurous acid*, consisting of sulphur, oxygen, and hydrogen, according to the equation— $\text{SO}_2 + \text{OH}_2 = \text{SO}_3\text{H}_2$ , or  $\text{SOH}_2$ . The aqueous solution acquires the taste and smell of the gas, and acts like a strong mineral acid.

In order to prepare a concentrated solution of sulphurous acid, we avail ourselves of the action which sulphuric acid exerts upon certain metals.

**Experiment 91.**—Introduce some copper clippings or turnings into a flask provided with a funnel-tube and two delivery-tubes (Fig. 57). Add a little concentrated sulphuric acid, and heat gently over a sand-bath. As long as the glass stopcock on the left hand side delivery-tube, which dips into a solution of soda, remains closed, the sulphurous anhydride, which is copiously evolved, is forced to pass through a Woulfe's bottle containing water (for the purpose of arresting any sulphuric acid fumes), into a second bottle containing distilled water. When the absorption of the gas ceases, and the glass stopcock on the left is opened, the gas can be made to pass into the soda solution contained in the cylinder on the left, which absorbs it freely. Remove the saturated solution of sulphurous acid, and keep it in a well stoppered bottle for further use.

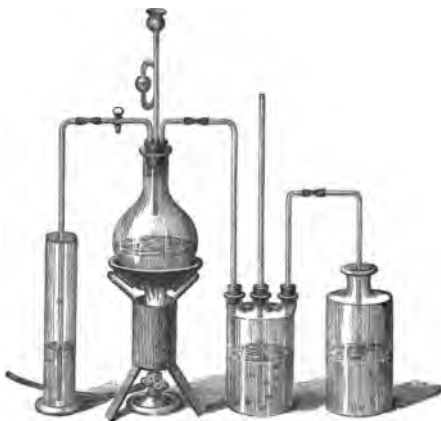
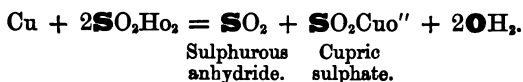


FIG. 57.—PREPARATION OF SULPHUROUS ACID.

The reaction takes place according to the equation :—



The oxidation of the copper is effected at the expense of the sulphuric acid, with evolution of one molecule of  $\text{SO}_2$ . A second molecule of  $\text{SO}_2\text{Ho}_2$  combines with the cupric oxide to form cupric sulphate, which is left behind in the flask, and which may be recovered by diluting with water, filtering, and evaporating, when it is left in the form of fine blue crystals ( $\text{SO}_2\text{Cuo}'', 5\text{OH}_2$ ).

Several other metals, *e.g.*, mercury and silver—metals, which, like copper, do not decompose water—might have been substituted for the metallic copper. Non-metallic bodies, such as carbon (and various organic bodies), sulphur, etc., can likewise effect a partial deoxidation of the sulphuric to sulphurous acid.

**Experiment 92.**—Substitute for the wash-bottle containing water (Fig. 57) a Woulfe's bottle charged with concentrated sulphuric acid, and pass the dried sulphurous anhydride through a U-tube, tapped at the bend and surrounded by a freezing mixture consisting of ice and salt, at  $-10^\circ \text{C}$ . The gas condenses readily to a colourless liquid of specific gravity 1.49, which becomes solid at  $-76^\circ$ . Draw off some liquid  $\text{SO}_2$ , into a test-tube, and watch for the deposition of a hoar-frost. Add a little water, and observe the freezing of the water, and the vaporisation of the sulphurous anhydride, by the heat which it suddenly abstracts from the water. Liquid sulphurous anhydride may be preserved in sealed tubes.

**Experiment 93.**—Collect some sulphurous acid by displacement (comp. Exp. 70) in a glass jar. Introduce a bunch of roses and stopper up the jar. The flowers will become *bleached*, but their colours are not destroyed, as was the case with chlorine gas, for on adding either an alkali (a dilute solution of ammonia) it is at first restored, and then changed to a green; or, on the addition of a stronger acid (sulphuric), the colour is again restored.

The same may be shown by means of an infusion of red cabbage leaf or log-wood.

**Experiment 94.**—Add to a solution of sulphurous acid, drop by drop, a solution of potassic permanganate (mineral chamæleon), and observe that the colour of the latter is permanently destroyed, for neither alkalies nor acids can restore it.

The change depends in this case upon the oxidation of the sulphurous into sulphuric acid, whilst in the case of the vegetable colouring matters the acid does not appear to be acted upon, but seems rather to form colourless combinations with them. Stains of fruit, port, or claret, etc., can be removed from linen by treatment with a solution of sulphurous acid.

Woollen goods, silk, straw, sponge, isinglass (glue), are bleached by exposure, in a moist state, to the fumes of burning sulphur, or by immersion in a solution of the acid.

Sulphurous acid is likewise a powerful *disinfectant*. It is used for arresting fermentation in beer, wine, cyder, &c. An alcoholic solution of sulphurous acid is one of the most powerful disinfectants for sick-rooms.

Although oil of vitriol may be broken up into oxygen and sulphurous acid by allowing it to fall upon white-hot platinum, the combination of the sulphur dioxide,  $\text{SO}_2$ , with a third atom of oxygen, so as to form sulphur trioxide,  $\text{SO}_3$ , has to be effected by indirect means.

**Experiment 95.**—Expose a freshly prepared solution of sulphurous acid in a shallow vessel for some time to the oxidizing action of the air. Add then a few drops of a solution of baric chloride to the solution; a white precipitate of baric sulphate,  $\text{SO}_2\text{BaO}$ , insoluble in dilute hydrochloric acid, will be obtained, whilst the precipitate produced in the acid before exposure, consisting mainly of baric sulphite,  $\text{SOBaO}$ , is all but soluble.

**Experiment 96.**—Add a few drops either of nitric acid, of chlorine water, or hydroxyl, to another portion of the aqueous sulphurous acid, and test in like manner. A heavy insoluble white precipitate is left. Neither of these oxidizing agents give by themselves a precipitate with baric chloride.

Certain porous bodies, such as *platinum black* or *spongy platinum*, prepared by strongly heating platinic chloride ( $\text{PtCl}_4$ ), appear by a kind of *catalytic* action to facilitate the combination of a third atom of oxygen with the sulphurous acid, by condensing the two gases within their pores.

**Experiment 97.**—Charge a piece of combustion glass, drawn out at one end to an open point, as seen in Fig. 58, with spongy platinum (a coil of fine platinum gauze or even platinized asbestos). Heat the tube to a low red heat, and pass a slow current of  $\text{SO}_2$  and oxygen over it—two volumes of the former to one volume of the latter. In order to regulate the two currents approximately, the gases are each passed through a wash-bottle containing oil of vitriol, before they enter the empty three-necked Woulfe's bottle, where they mix (diffuse) previous to their passing over the spongy platinum.

Dense white suffocating fumes are formed in the tube, and as soon as the gas comes in contact with the moisture of the atmosphere on issuing from the tube (both oxygen and sulphurous anhydride are colourless gases), which, when passed

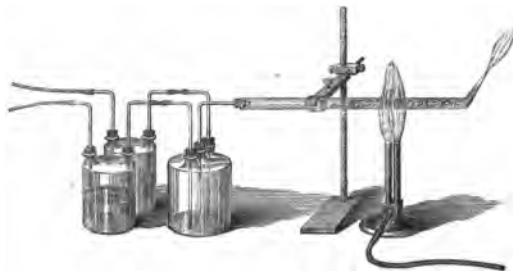
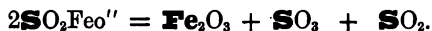


FIG. 58.— $\text{SO}_3$  PREPARED DIRECTLY FROM  $\text{SO}_2$  AND OXYGEN.

into water, are absorbed. Hold a gas jar (comp. Exp. 6), moistened inside with water, or a dilute solution of ammonia, for a few minutes over the jet, and then test the condensed acid or solution of the ammoniac salt by means of a solution of baric chloride. A dense white insoluble precipitate of baric sulphate is obtained. Filter and add some chlorine water to the clear filtrate. No farther precipitate (comp. Exp. 96) comes down. The whole of the sulphurous anhydride has been converted in the experiment into sulphuric anhydride, thus:—

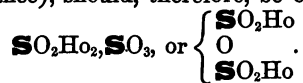


The strongest sulphuric acid, so-called *Nordhausen acid*, from a town in Saxony, where it was mainly manufactured, is obtained by distilling well dried ferrous sulphate (*green vitriol*) in earthenware retorts, and condensing the acid fumes in glass or earthenware vessels. Heat liberates the acid, leaving  $\text{Fe}_2\text{O}_3$  as a red powder, known as *colcothar (rouge)*, which is used for polishing plate glass, metals, &c. The change is pretty correctly expressed by the equation:—



Sulphuric Sulphurous  
anhydride. anhydride.

Some sulphuric acid is, however, always formed, since the whole of the water is in practice never driven off entirely from the green vitriol ( $\text{SO}_2\text{Feo}''$ ,  $7\text{OH}_2$ ) before it is submitted to destructive distillation, and the composition of the acid (called *oil of vitriol*, from its oily appearance), should, therefore, be expressed by the formula



This process, discovered four centuries ago by the German alchemist Basil Valentine—a discovery which had the greatest influence upon the progress of chemistry—has now been almost entirely superseded by the so-called *English process* of manufacturing sulphuric acid. The reactions involved in this latter process will be explained when a knowledge of the oxides of nitrogen has been acquired.



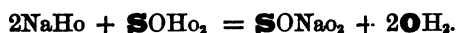
Concentrated sulphuric acid is a powerful *dehydrating* agent. It chars almost all organic substances by depriving them of their hydrogen and oxygen (or water). When mixed with water it gives out great heat, so that much care should be observed in diluting the strong acid.

**Experiment 98.**—Pour a little of the strong acid over some wooden shavings. The wood becomes blackened almost instantaneously.

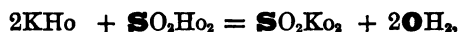
**Experiment 99.**—Add one volume of concentrated sulphuric acid to two volumes of strong syrup of sugar placed in a capacious beaker on a plate; stir up quickly. The liquid becomes intensely hot, and swells up to a bulky, black, porous mass of finely divided charcoal.

Sugar consists of  $C_{12}H_{22}O_{11}$ , and is broken up by the acid into 12 atoms of carbon and 11 molecules of water, which combine chemically with the sulphuric acid. Hence the great heat which accompanies the chemical change.

Both sulphurous and sulphuric acid, by combining with salifiable bases, form most important salts, called *sulphites* and *sulphates*,—*neutral* if the whole of the hydrogen of the acids is replaced by a metal, as *e.g.* :—

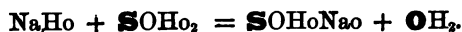


Sodic sulphite.



Potassic  
sulphate.

*acid*, if only one-half of the hydrogen is displaced, *e.g.* :—



Acid, or hydric  
sodic sulphite.



Acid, or hydric  
potassic sulphate.

Potassic sulphate, like sodic chloride, has neither acid nor basic properties; it is an indifferent or neutral body. Sulphates of the alkali metals are soluble in water. Baric sulphate is practically insoluble in water as well as in dilute acids; strontic, calcic, and plumbic sulphates nearly so, argentic sulphate is difficultly soluble in water. All other metallic sulphates are soluble in water.

Metallic sulphates can, with few exceptions, be prepared—

1st. *By the action of sulphuric acid upon the metals,\**

(a) *with evolution of hydrogen* when the acid is dilute, *e.g.*, K, Na, Ba, Sr, Ca (the last three metals are imperfectly acted upon on account of the formation of insoluble sulphates). Mg, Al (requires the application of heat) **Fe''**, **Zn''**, Cd,

\* Practically no others than the metals printed in thick type would ever be dissolved in sulphuric acid for the purpose of preparing their sulphates.



ternary compounds called *oxy-salts*, because three elementary bodies enter into their composition, one of which is always oxygen.

Salts may thus be divided into—

1. *Haloid salts* (binary compounds), *e.g.*, chlorides (bromides, iodides), etc.
2. *Oxy-salts* (ternary compounds), *e.g.*, sulphates, sulphites, and many others,

and the same nomenclature is used in the case of *oxy-salts* which was adopted for haloid salts, viz., the name of the metallic element is employed adjectively, and that of the acid substantively; the name of the acid element of *oxy-salts* ending, however, as in potassic sulphate and sodic sulphite in *ate* and *ite*, in order to distinguish them from the acid element of haloid salts which terminate in *ide*, as potassic chloride.

#### QUESTIONS AND EXERCISES.

1. You have given to you an alloy of silver and copper (*e.g.*, a sixpenny piece) and sulphuric acid. State what chemical compounds can be produced from these materials. Express the changes by equations.
2. Describe how you would prepare liquid sulphurous acid.
3. How would you demonstrate the bleaching and disinfecting action of sulphurous acid? Give an explanation of it.
4. How is sulphurous acid acted upon by air, by nitric acid, by hydric peroxide?
5. Describe how  $\text{SO}_2$  and oxygen gas can be made to combine directly with each other?
6. How is Nordhausen sulphuric acid obtained?
7. Explain the action of concentrated sulphuric acid upon wood or syrup of sugar.
8. How would you prepare neutral and acid sodic sulphite or potassic sulphate?
9. Describe methods for preparing magnesian sulphate, mercuric, and zincic sulphates. Express the changes by equations.
10. Explain what nomenclature has been adopted for distinguishing haloid from *oxy-salts*. Give illustrations.
11. Practise symbolic and graphic formulæ of the following compounds: sulphurous acid, hydric sodic sulphite, calcic sulphate, magnesian sulphite, ferrous and ferric sulphates, argentic sulphite.

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#### CHAPTER XV.

### CARBON, its Properties.—CARBONIC ANHYDRIDE, CARBONIC OXIDE.—CARBONATES.

*Carbon* is one of the most important elements with which we are acquainted. It occurs in nature mainly in combination with other elements, such as oxygen, hydrogen, etc. It constitutes the essential element of everything *organic*, both of vegetable and animal origin. We are familiar with three varieties—three so-called *allotropic* forms of carbon, viz., (1) *amorphous* carbon—mineral and artificially prepared

charcoal, coke, etc., (2) *graphite* or black-lead (plumbago), "kish," the graphitic carbon which often separates from melted pig-iron, and (3) *diamond*, the hardest of known substances, consisting of crystallised carbon, brilliant, transparent, and generally colourless. In all these forms carbon is infusible and non-volatile, and apparently unalterable in the air and in water at ordinary temperatures. Combined with oxygen and hydrogen, a little nitrogen and sulphur, and more or less mineral matter (ash), it constitutes some of the most important natural substances, such as *anthracite* (*culm*), containing 90—94 per cent. of carbon and but little volatile matter; house or *pit coal*, containing varying quantities (from 80—90 per cent.) of carbon, varying through cannel and bituminous coals of numerous varieties down to *lignite* or *brown coal*, which still bears the imprint of the fibrous structure of the wood from which it is derived.

**Experiment 100.**—Heat a small piece of wood in a test-tube, loosely kept closed with the thumb, and observe the changes. Some water and tarry matter pass off, which condense in the upper part of the tube, as well as some gaseous matter, which burns with a bright flame, and the wood will be found to be converted into *charcoal*.

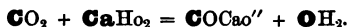
By heating bituminous coal out of contact with air, in so-called coke-furnaces, or, for the purposes of manufacturing coal-gas, in long iron or clay retorts, a large quantity of gas and of tar distils off, which are either for the most part consumed in the coke furnace or systematically collected, and the gas stored up in gas-holders for illuminating purposes. The *coke* which is left in these processes of *destructive distillation* constitutes a porous mass of carbon, resembling graphite in its properties, but retaining all the mineral impurities of the coal. *Animal charcoal* or *bone-black*, another variety of less pure carbon, is obtained by heating bones in iron retorts. It contains about 90 per cent. of mineral matter (calcic phosphate), and is largely used by sugar refiners as a *decolorising agent*.

Ordinary wood charcoal, as well as animal charcoal, possesses a remarkable power of absorbing gases, owing to its great porosity. The latter especially is used as an energetic *disinfecting agent*. Foul gases are oxidized by being brought, within its pores, in close contact with the atmospheric oxygen.

We have already become acquainted with a gaseous compound of carbon and oxygen, called *carbonic anhydride*, obtained by burning carbon in air or oxygen (Exp. 24), and have experimentally established, both synthetically (Exp. 24) and analytically (Exp. 32), that these two elements enter into its composition. Traces of this gas are invariably found in the air; the amount varies from .03 to .06 per cent. in pure air, and from  $3\frac{1}{2}$  to 4 per cent. in air which passes from our lungs.

**Experiment 101.**—This may be shown by exposing some clear lime-water in a shallow glass dish to the air, when it will speedily become covered with a white pellicle of calcic carbonate or chalk (comp. Exp. 27); or by blowing the breath, by means of a glass tube, from the lungs through lime-water. The

latter will even more speedily become turbid, owing to the formation of calcic carbonate. The reaction is expressed by the equation—



Respiration in animals is always attended with the formation of carbonic anhydride. Combustion of organic (or carbon) substances, slow decay, fermentation of saccharine matter, etc., likewise give rise to its evolution, and the gas would go on accumulating in the air were it not for growing plants, which under the influence of sunlight decompose it by storing up the solid carbon and setting free the oxygen, and for the rain, etc., which carries it down again to the earth into springs and rivers, wherewith to feed and nourish the roots of the plants. Water, beer, champagne, lemonade, etc., owe their briskness and freshness to the presence of more or less carbonic anhydride which they hold in solution. Soda-water is spring water charged with the gas under pressure. At the ordinary temperature, and without any pressure, water absorbs about its own bulk of it.

The setting and hardening of ordinary mortar (slaked lime

mixed with more or less sand) is due to a great extent to the absorption of carbonic anhydride and the slow conversion of the caustic into carbonated lime or chalk. From this source, as well as from certain mineral bodies containing it, such as chalk, marble, it may be readily obtained by the action of hydrochloric or other acid.

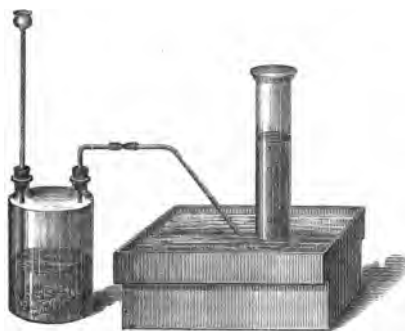


FIG. 59.—PREPARATION OF CARBONIC ANHYDRIDE.

and add through the funnel-tube dilute hydrochloric acid. Effervescence ensues, and a colourless gas comes off. Fresh acid is added from time to time, as long as any marble is left undissolved. The reaction is expressed by the equation—



Calcic  
carbonate.

Calcic  
chloride.

We can readily collect some of the gas over water in glass cylinders, and have no difficulty in recognising it as carbon dioxide or carbonic anhydride, since it is acid to litmus-paper, extinguishes a light, is heavier than air, and gives a white precipitate with lime or baryta-water. Its specific gravity compared with air is  $\frac{1.529}{1.293} = 22$ , when compared with hydrogen. One litre of the two-

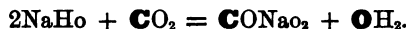
\* Instead of this simpler apparatus, we may also employ the apparatus described in Exp. 54, and secure thus a constant supply of  $\text{CO}_2$ .

volume vapour carbonic anhydride, consisting of one atom of carbon and two atoms of oxygen, weighs  $\frac{12 + 2 \times 16}{2} = 22$  times as much as a litre of hydrogen, or 22 criths, *i.e.*,  $22 \times .0896 \text{ grm.} = 1.9712 \text{ grm.}$  The molecular weight of carbonic anhydride is therefore 44. It is written graphically  $\text{O}=\text{C}=\text{O}$ , carbon being a tetrad element.

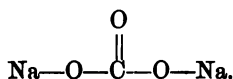
Subjected to a pressure of  $38\frac{1}{2}$  atmospheres at  $0^\circ \text{C.}$ , it condenses to a colourless limpid liquid of specific gravity .83, and by allowing a fine jet of the liquefied gas to issue into the air, the rapid evaporation of one portion freezes another, producing a snow-white flocculent solid mass, which may be formed into balls like snow.

The density of gaseous carbonic anhydride may be illustrated in various amusing ways. The gas may be poured from one vessel into another, drawn off by a syphon, ladled out, poured into a glass vessel accurately counterbalanced on a pair of scales; soap bubbles of air may be made to float and rebound on its surface, etc.

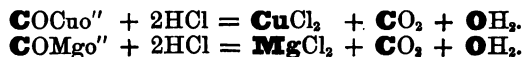
**Experiment 103.**—Pass some carbonic anhydride into a solution of caustic soda,  $\text{NaHo}$ . The gas is absorbed. On evaporating the solution to dryness, and igniting gently in a porcelain dish, then dissolving the dry mass once more in hot water, crystals of a salt are obtained, which analysis has shown to be composed of three elementary bodies, *viz.*, sodium, carbon, and oxygen. Its formation is explained by the following equation:—



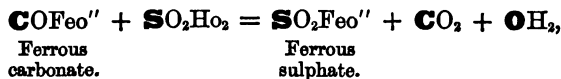
The salt is disodic carbonate, and is one of a large and important class of salts called *carbonates*. The tetrad element carbon forms the grouping element, its bonds being satisfied by one atom of dyad oxygen, and two of the monad radical sodoxyl,  $\text{NaO}$ . It is expressed graphically:—



We have now to add one more method to the four methods enumerated above for preparing metallic chlorides, etc., *viz.*, by the action of dilute hydrochloric acid upon metallic carbonates, *e.g.*—



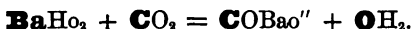
It is obvious that metallic sulphites and sulphates may, in like manner, be prepared from metallic carbonates, by treating the latter with dilute sulphuric acid, etc., *e.g.*—



and as many metals occur in nature more or less abundantly in the form of carbonates (*e.g.*, K, Na, Ba, Sr, Ca, Mg, Fe, Zn, Mn, Pb,

Cu), this method of preparing chlorides, sulphites, and sulphates, and, as we shall shortly see, other salts also, will at once recommend itself as the most convenient and cheapest, especially as carbonates are, for the most part, decomposed with great facility even by weak organic acids, such as acetic or tartaric acid.

**Experiment 104.**—Pass carbonic anhydride gas through a solution of baric hydrate,  $\text{BaHO}_2$ . The gas is likewise absorbed, and a white precipitate falls as soon as the first bubbles of the gas are passed into the solution. The precipitation ceases after a while, and by filtering off the white powder, which consists of barium, carbon, and oxygen, we obtain a salt called baric carbonate, insoluble in water. Its formation is expressed by the equation—



On passing carbonic anhydride gas somewhat longer through the solution in which some of the precipitate is suspended, the latter disappears, and the liquid becomes once more clear. Excess of carbonic anhydride, then, dissolves the baric carbonate (comp. Exp. 27).

It combines, in fact, with the caustic alkalies and alkaline earths in two proportions, forming either a neutral carbonate or an acid, or hydric carbonate respectively.

The carbonates of the alkali metals are soluble in water, all other (neutral) carbonates are insoluble.

One more compound only of carbon with oxygen exists, and claims a brief notice, viz., *carbonic oxide*, " $\text{C}''\text{O}$ ", containing just half as much oxygen as the oxide already described.

**Experiment 105.**—Pass a slow current of carbonic anhydride over lumps of charcoal contained in a porcelain (or iron) tube, and heated in a charcoal furnace, as seen in Fig. 49, or a Hofmann's gas furnace. Collect the gas in glass cylinders over water as it issues from the tube. Apply a light to the mouth of the cylinder: the gas will burn, at the mouth of the cylinder only, with a fine blue flame characteristic for carbonic oxide gas.

The carbonic anhydride is deprived of half its oxygen by being brought into contact with ignited carbon, and becomes converted into carbonic oxide:  $\text{C}^{\text{iv}}\text{O}_2 + \text{C} = 2''\text{C}''\text{O}$ , in which two bonds of the element carbon have become latent. The volume of the gas is exactly doubled.

This experiment explains some of the chemical changes we observe in ordinary coal fires, in blast furnaces, etc.

Instead of preparing carbonic oxide by the action of carbon upon carbonic anhydride, it is usually prepared for laboratory purposes by breaking up certain carbon compounds, by acting upon them with sulphuric acid.

**Experiment 106.**—Heat in a flask (Fig. 60) some crystallised oxalic acid with about 10 times its weight of oil of vitriol. Pass the gaseous mixture, which consists of  $\text{CO}$  and  $\text{CO}_2$ , through a wash-bottle containing a solution of caustic soda, in order to absorb the  $\text{CO}_2$  (comp. Exp. 103), and collect the carbonic oxide over water.

Oil of vitriol is, as we know, a powerful dehydrating agent, and by abstracting water from the oxalic acid the remnant  $\text{C}_2\text{O}_3$  immediately breaks up into  $\text{CO} + \text{CO}_2$ . The reaction is expressed by the equation :—

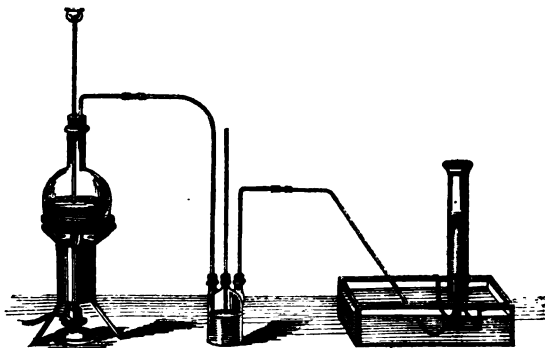
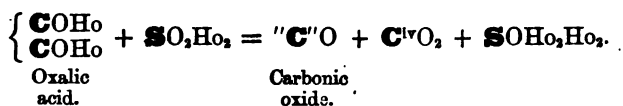
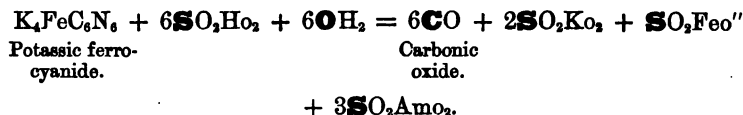


FIG. 60.—PREPARATION OF CARBONIC OXIDE.

**Experiment 107.**—Another method of preparing this gas consists in heating some sharply dried potassic ferrocyanide (or yellow prussiate of potash) with about 10 times its weight of oil of vitriol. Employ a flask with a wide delivery tube, as the gas comes off after a time very quickly. Collect over water.

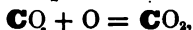
The composition of yellow prussiate is expressed by the somewhat complicated formula,  $\text{K}_4\text{FeC}_6\text{N}_6, 3\text{OH}_2$ . On heating the dried salt together with sulphuric acid, it breaks up into pure carbonic oxide, while the whole of its nitrogen remains behind as ammoniac sulphate, and the potassium and iron likewise as sulphates. The reaction may be expressed by the equation:—



**Experiment 108.**—Inflame a cylinder of carbonic oxide, and introduce a lighted taper. The light will be extinguished, but the gas will continue to burn, at the mouth of the cylinder, with a blue flame. It departs itself in this respect like hydrogen gas (comp. Exp. 3). Add now a little lime-water and shake up. A white precipitate of chalk will be produced.

**Experiment 109.**—Add lime-water to another cylinder filled with the gas, without previously inflaming it. Shake up. No precipitate will be produced.

This shows that carbonic anhydride has been produced by the combustion of carbonic oxide in air. Two vols. of  $\text{CO}$  require one vol. of  $\text{O}$ , according to the equation:—



and are converted into 2 vols. of  $\text{CO}_2$ , i.e., the 3 volumes of the two gases contract into 2 volumes.



Carbonic oxide has a specific gravity of .967, as compared with air, or  $\frac{.967}{.0691} = 14$ , when compared with hydrogen. One litre of

the two volume gas weighs  $\frac{12 + 16}{2} = 14$  times as much as a litre

of hydrogen, or 14 criths, *i.e.*,  $14 \times .0896 \text{ grm.} = 1.2544 \text{ grm.}$  The molecular weight of carbonic oxide is 28. This gas has not been liquefied. It is but little soluble in water (1 vol. of the gas dissolves in 40 vols. of water). It is colourless, possesses a faint oppressive odour, is totally irrespirable, and is very poisonous. One part of the gas in 100 parts of air speedily produces a sensation of giddiness, and when inhaled for any length of time proves fatal. Carbonic oxide dissolves slowly when agitated with a hydrochloric acid solution of cuprous chloride,  $\text{Cu}_2\text{Cl}_2$ . Both carbonic oxide and dioxide are normal constituents of coal gas.

Carbon forms a compound also with nitrogen, called *cyanogen*, with sulphur, with hydrogen,—the so-called *hydrocarbons* which belong to organic chemistry,—also compounds with many metals, termed *carbides*. The study of these compounds must, however, be left to a course of lectures.

#### QUESTIONS AND EXERCISES.

1. How does the element carbon occur in nature?
2. Describe the allotropic modifications of carbon.
3. Explain the action of heat upon wood, coal, coke, in close vessels.
4. Explain the decolorising and disinfecting action of wood and animal charcoal.
5. What changes take place when carbonic anhydride is successively passed into distilled water, into solutions of baric or calcic hydrate?
6. Describe several sources of carbonic anhydride.
7. Find the volume weight of carbonic anhydride, and calculate the weight of 66.5 c.c. of the dry gas.
8. You pass 6 litres of oxygen over 5 grms. of carbon (charcoal). How much carbonic anhydride by volume and by weight can you obtain by the combustion of the carbon in oxygen, and how much carbon, if any, will be left?
9. How much carbon will be required to convert 10 litres of carbonic anhydride into carbonic oxide, and what will be the volume of the gas so obtained.
10. How much carbonic anhydride by weight and by volume will be required to convert 2.5 grms. of  $\text{Na.Ho}$  into disodic carbonate?
11. Give the symbolic and graphic formulæ of the following compounds: carbonic anhydride, carbonic oxide, baric carbonate, argentic carbonate, ferrous carbonate, hydric potassic carbonate.
12. Describe several methods for preparing pure carbonic oxide. Give equations.
13. How would you experimentally distinguish  $\text{CO}_2$  from  $\text{CO}$ ?
14. Describe the distinctive properties of both gases.
15. Explain the terms: *plumbago*, *culm*, *kish*, *coke*, *lignite*, *animal charcoal*, *mortar*, *choke damp*, *yellow prussiate*, *cyanogen*, *hydrocarbon*, *carbide*.

## CHAPTER XVI.

## THE OXIDES OF NITROGEN. MANUFACTURE OF SULPHURIC ACID.

Two important compounds containing one of the oxides of nitrogen in combination with the alkali metals potassium and sodium exist in nature, and are known to us as *potash nitre* (or *saltpetre*) and *soda nitre* (*Chili saltpetre*, *cubic nitre*). The affinity which nitrogen possesses for oxygen is so feeble, that in atmospheric air (which consists of a mixture of these two gases) they exist side by side without combining; and it is only by the most powerful agencies (such as electrical discharges) that very trifling quantities of an acid product of oxidation can be obtained. Nitre is principally found in tropical countries, where the rapid oxidation of certain organic nitrogenized bodies, such as animal excrements, and especially urine, under the influence of a hot tropical sun, notably in presence of porous lime soils and soils rich in alkalies, produces this most important of nitrogen compounds in considerable quantities. We know of no reactions by which the oxides of nitrogen could be formed directly from their elements in appreciable quantities. The affinity which draws their component atoms together being found very feeble, their power of resisting decomposition is proportionally weak; and hence it is that these compounds part readily with their oxygen, and that the different oxides of nitrogen are among the most powerful *oxidizing* agents known.

The combustibility of a gas depends upon whether we can raise it to a sufficiently high temperature to cause it to ignite, *i.e.*, to combine chemically with oxygen, etc., in other words whether it has a low or high *ignition point*. By employing the electric spark (which may be said to be as much hotter again, as a blast furnace is compared with ice) we can succeed in combining nitrogen with oxygen.

**Experiment 110.**—Pass the electric spark through a mixture of nitrogen and oxygen, or through moist air, contained in a tri-tubulated glass globe (Fig. 61). Increase the pressure by connecting the open glass-tube with a forcing pump, since gases are known to burn more readily and with intenser light when under pressure. Place some damp blue litmus-paper into the glass-globe. In 5 to 10 minutes from the time when the electric spark has been first sent through the gaseous mixture, red fumes are observed and the blue litmus-paper is seen to turn red. An acid results from the combination of the two gases, called *nitric acid*.

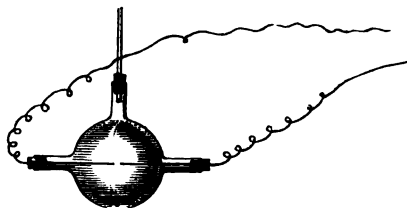


FIG. 61.—COMBINATION OF OXYGEN AND NITROGEN BY ELECTRIC DISCHARGES.

Rain-water generally contains traces of nitrous and nitric acid in the form of ammoniacal nitrite and nitrate, owing to the action of lightning or atmospheric electricity. The quantities so found are greater in tropical countries, where electrical discharges in the air are more frequent and more powerful.

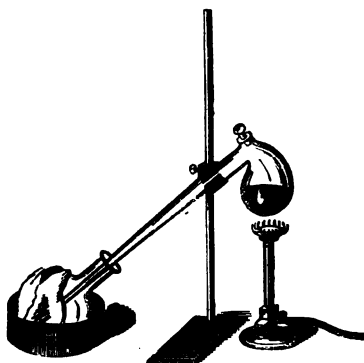
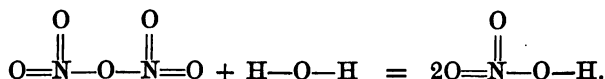


FIG. 62.—PREPARATION OF NITRIC ACID.

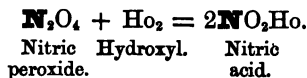
**Experiment 111.**—Introduce into a small retort (Fig. 62) a little nitre with sufficient concentrated sulphuric acid to cover the salt. Carefully prevent the acid and the salt from coming in contact with the neck of the retort.

Apply gentle heat. A reaction is seen to take place, and ruddy vapours come off which condense in the neck of the retort. The receiving flask should be kept cool by partially immersing it in a basin of cold water, and by covering it with a wet cloth or filter-paper. The distillation continues briskly for some time, and an orange-red liquid condenses in the receiver. The operation may be discontinued when no more ruddy vapours are observed in the body and neck of the retort.

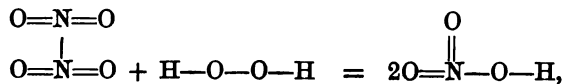
The liquid in the receiving flask reddens blue litmus instantaneously. It is an acid body called nitric acid. Analysis has proved that it is a ternary body, composed of nitrogen, oxygen and hydrogen, viz.,  $\text{N}_2\text{O}_5\text{H}$ . Nitrogen being, however, a pentad element, it follows that in  $2\text{NO}_3\text{H}$ , which we may view as obtained by the combination of one molecule of  $\text{N}_2\text{O}_5$  with one molecule of  $\text{OH}_2$ , six atoms of dyad oxygen and two atoms of monad hydrogen cannot be united directly to two atoms of nitrogen; but that the two atoms of hydrogen link themselves to two atoms of oxygen to form two semi-molecules of the compound radical hydroxyl. This may be shown graphically as follows:—



Or, if we view nitric acid as the result of the direct combination of the next lower oxide of nitrogen,  $\text{N}_2\text{O}_4$ , or nitric peroxide (the preparation of which will be explained below), with one molecule of the compound radical hydroxyl,  $\text{Ho}_2$ , the equation will be—

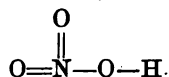


or expressed graphically—



we find that one molecule of anhydrous  $\text{N}_2\text{O}_5$ , or one molecule of  $\text{N}_2\text{O}_4$ , must give rise to two molecules of nitric hydrate or nitric acid, the atom group  $\text{NO}_2$  remaining unchanged, like the group  $\text{SO}_2$ , in  $\text{SO}_2\text{Ho}_2$ .

The pentad element nitrogen links together two atoms of dyad oxygen as well as the monad radical hydroxyl, and we therefore write the graphic formula of nitric hydrate or nitric acid—

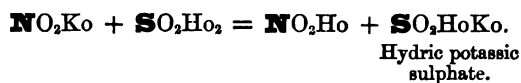


The distillate collected in the receiving flask consists of a more or less concentrated solution of nitric acid. It attracts moisture from the air and holds it chemically combined, yielding it up again only by round-about processes, and not without suffering partial decomposition.

On warming the flask ruddy fumes of a suffocating and poisonous nature are given off, and the remaining liquid becomes colourless or nearly so. The volatile gaseous portion consists of lower oxides of nitrogen. It is evident therefore that the affinity which nitrogen possesses for oxygen in nitric acid is not sufficient even to resist its partial decomposition upon simple distillation.

The liquid remaining in the retort solidifies on cooling to a saline crystalline mass of hydric potassic sulphate. It is possible under given conditions, *e.g.*, excess of acid, to obtain a sulphate in which only half the Ho is replaced by Ko. The nitric acid also comes off at a considerably lower temperature, and is therefore less coloured by lower oxides of nitrogen—the products of the decomposition of nitric acid. Such a salt is called an *acid salt*. Only dibasic or dihydric acids are capable of forming acid salts. Monobasic acids (such as nitric acid), containing one replaceable Ho, can only form one kind of salts.

The action of sulphuric acid upon nitre or potassic nitrate is expressed by the equation—

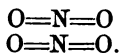


A more dilute nitric acid formed from one molecule of  $\text{N}_2\text{O}_5$ , and four molecules of water is a much more stable liquid. The degree of hydration in the case of nitric acid, as in that of other acids, is generally not expressed by the formula assigned to the dilute acid.

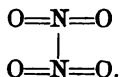
The strongest nitric acid is a fuming, intensely corrosive liquid, which stains the skin yellow and destroys the epidermis. It has a specific gravity of 1.52. Cooled to about  $-40^\circ \text{C}$ ., it freezes, and heated to  $85.5$  it boils, suffering partial decomposition. Many organic non-nitrogenous bodies, such as cotton, glycerin, sugar, benzol, carbolic acid, are converted by it into violently-explosive bodies. The acid of 1.42 sp. gr. has a definite boiling point of  $120.5^\circ$ , but is not, therefore a definite hydrate.



and as the  $N_2$  in nitric peroxide forms a chemical compound with  $O_4$ , it is obvious that the nitrogen atom could no longer be penta-valent, as four atoms of dyad oxygen cannot satisfy the combining powers of two atoms of pentad nitrogen. It is also apparent that if nitrogen acted as a tetrad element in nitric peroxide there would be no connection between the two atoms of nitrogen, thus:—



It is therefore probable that the connection between the two nitrogen atoms still exists, even without the intervening oxygen atom, and that nitrogen retains its pentad nature, thus:—



The fact that the atom of oxygen which linked together the two groups of  $NO_2$  in  $N_2O_4$  is so easily driven out by heat, shows—

3. That a marked difference exists between the chemical affinity which the two atoms of nitrogen in nitric anhydride exhibit for the different atoms of oxygen.

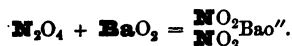
The yellow liquid collected in the U-tube boils at  $22^\circ C.$ , and solidifies to a mass of colourless crystals at  $-13^\circ C.$  The crystals dissolve at first to a colourless liquid, which turns yellow as the temperature rises, and becomes at last red. Blue litmus-paper is turned red by the puffs of ruddy vapour expelled from the liquid; and the compound  $N_2O_4$  was therefore thought to be an acid body, and was called hyponitric acid. This reddening of the litmus is, however, due to the water in the paper, with which nitric peroxide undergoes a decomposition, and the name *hyponitric acid* is quite inappropriate. A most interesting change takes place when the ruddy vapour is passed into a solution of potassic hydrate. Complete absorption of the gas takes place, and the liquid loses its alkaline properties. On examining the products thus formed, we find two different salts, potassic nitrate,  $NO_2Ko$ , and potassic nitrite, of the composition  $NOKo$ . The acid corresponding to this latter salt contains one atom of oxygen less than nitric acid. It is called *nitrous acid*,  $NOHo$ . The change may be expressed by the equation—



Nitrous acid, on combining with bases, forms well characterised salts, called *nitrites*. In the free state, however, it is extremely unstable. It cannot be preserved at the ordinary temperature, without undergoing decomposition, according to the equation:—

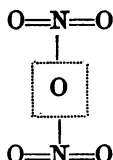


**Experiment 113.**—If instead of potassic hydrate (or, as we may also view it, potassic water) a solution of peroxide of hydrogen, or some other metallic peroxide, be added to nitric peroxide, we obtain at once nitric acid, or a corresponding metallic nitrate, according to the equation—

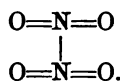


The following considerations render it probable that three atoms of oxygen in nitric anhydride are held less firmly by the nitrogen atoms than the other two atoms of oxygen.

In the molecule of nitric anhydride represented graphically by the formula—

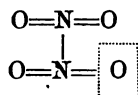


the oxygen atom in the dotted square is the first to go out, leaving the molecule  $\left\{ \begin{array}{l} \mathbf{NO}_2 \\ \mathbf{NO}_2 \end{array} \right.$  (nitric peroxide).

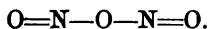


In both formulæ nitrogen acts the part of a *pentad* element.

Nitric peroxide would appear to contain an atom of oxygen less firmly united with the nitrogen atom, such as the oxygen atom which has been placed within a dotted square—



In the molecule of nitrous anhydride,  $\mathbf{N}'''\mathbf{O}_2$ , nitrogen is a *triad* element, two of its bonds becoming latent, thus:—

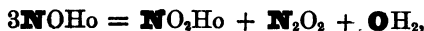


It is evident from a glance at this formula that the oxygen atoms of nitric peroxide must rearrange themselves, for we have again an atom of oxygen linking together the two nitrogen atoms, as in nitric anhydride.

In consequence of the unstable nature of free nitrous acid, it can be employed for purposes either of oxidation or reduction. Nitric peroxide breaks up according to the equation—



and nitrous acid according to the equation—



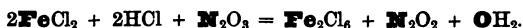
leaving as the ultimate products of decomposition of nitric peroxide only nitric acid and a colourless gas called nitric oxide,  $\text{N}_2\text{O}$ .

**Experiment 114.**—In order to illustrate experimentally the reducing and oxidizing action of nitrous acid (or of a nitrite mixed with a dilute acid, even acetic acid), a little nitrous anhydride may be prepared by acting with nitric acid upon lumps of arsenious anhydride, heated in a small flask, according to the equation :—



The gas may be collected by displacement, or over mercury.

**Experiment 115.**—Add a few c.c.'s of a slightly acidulated solution of ferrous chloride to a cylinder full of nitrous anhydride, and shake up. The light green solution becomes dark brown, owing to the absorption of  $\text{N}_2\text{O}$ , by a portion of the unoxidized ferrous salt, which forms with this latter an evanescent molecular compound. On the application of heat to the brown liquid, nitric oxide is evolved, and the solution of the salt becomes light yellow. The reaction may be expressed thus :—



Organic colouring matters, such as magenta or indigo solutions, reduce nitrous anhydride likewise to a lower oxide, to nitric oxide.

**Experiment 116.**—Add a slightly acidulated (sulphuric acid) solution of potassic permanganate to another cylinder of the gas. The colour of the permanganate is immediately destroyed. The  $\text{N}_2\text{O}$  is oxidized into nitric acid by the more powerful oxidizing agent, potassic permanganate.

These two experiments may equally well be performed by employing a solution of potassic nitrite in the place of the nitrous anhydride.

**Experiment 117.**—Introduce some copper turnings or clippings into a two-necked Woulfe's bottle, provided with a funnel and delivery-tube (Fig. 63). Nitric acid, diluted with about half its bulk of water, is then poured through the funnel into the bottle, which may be placed in a basin of cold water. The evolution of red fumes soon begins, and the air is gradually displaced by the gas. The red fumes within the bottle disappear (a sign that the air has been displaced), and at last the gas which comes off appears quite colourless. As soon as the gas which issues from the delivery-tube comes in contact with the air, it turns reddish brown. The fumes of this reddish brown gas are injurious when inhaled; the experiment must therefore be conducted in the open air or in a closet with sliding windows, and in a good draught. A glass cylinder is now filled with water, rendered slightly alkaline by means of a few drops of sodic hydrate (in order to absorb any fumes of nitric acid that may be carried over) and inverted over the shelf of the pneumatic trough, and the gas collected in the usual manner by the displacement of the water in the cylinder. A perfectly colourless gas is thus

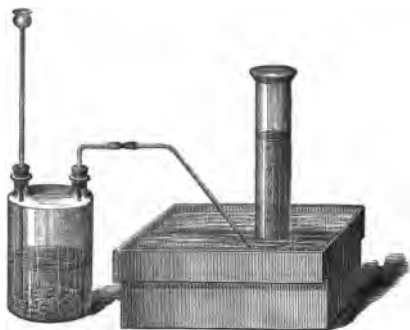


FIG. 63.—PREPARATION OF NITRIC OXIDE.



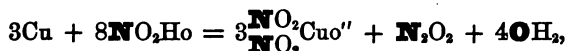
obtained. The cylinder, when full, is closed under water by means of a glass plate, and then removed with its gaseous contents. On introducing several folds of litmus-paper moistened with water which has been rendered slightly alkaline by means of a few drops of sodic hydrate, the gas turns instantaneously reddish-brown at the mouth of the cylinder, where it comes in contact with the air. The blue litmus is seen to turn red as rapidly as the ruddy fumes form. When the cylinder has been filled half way down with these fumes, the glass plate is replaced, and the lower part of the folds of litmus-paper is seen to remain blue in the colourless portion of the gas, whilst the upper part turns intensely red.

This experiment proves that the colourless gas obtained by the action of copper upon nitric acid is not an acid body, and that by mere contact with air it is converted into reddish-brown acid fumes, which are absorbed by water or by sodic hydrate. Since the oxygen and moisture of the air convert the colourless gas into an acid with which we have already become acquainted (*viz.*, into nitrous acid), it is reasonable to suppose that the colourless gas is likewise an oxide of nitrogen, containing, however, less oxygen than nitrous acid: and since it does not react acid, it can only be one of the two remaining oxides, *i.e.*, it must be either  $\text{N}_2\text{O}$ , or  $\text{ON}_2$ . Now quantitative experiments have shown that the gas is composed of two atoms of nitrogen and two atoms of oxygen. It is written symbolically and graphically—



an atom of nitrogen being linked to another atom of nitrogen, leaving two more bonds free in each, which are satisfied by an atom of dyad oxygen.

The reaction\* which took place when copper was treated with nitric acid must, therefore, be expressed by the following equation:—



and the deoxidation of a molecule of  $\text{N}_2\text{O}_4$ , which we have previously seen accomplished, step by step, first to  $\text{N}_2\text{O}_3$ , then to  $\text{N}_2\text{O}_2$ , and lastly to  $\text{N}_2\text{O}$ , is in this reaction attained at one leap.

Nitric oxide is remarkable for its great affinity for oxygen, and may be employed in testing for that gas.

**Experiment 118.**—Collect some of the gas in a glass cylinder over warm water, rendered very slightly alkaline with soda, and coloured blue with litmus. The blue solution remains unchanged. Now pass a few bubbles of oxygen or air from a gas-holder up into the nitric oxide; deep ruddy fumes will be immediately formed, which are, however, quickly dissolved by the alkaline water, and the blue solution becomes red. If both the oxygen and the nitric oxide are perfectly pure, it is possible to effect a complete oxidation of the nitric oxide into nitrous and nitric acid, and to cause a perfect absorption of the two gases.

**Experiment 119.**—Plunge a burning taper into a jar of nitric oxide gas. The

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\* There is invariably some ammonia ( $\text{NH}_3$ ) formed in this and other similar reactions, and it would appear, therefore, that water, under favourable circumstances, takes part in the change.

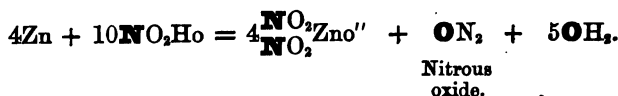
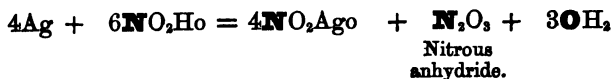
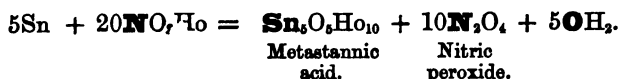
taper is immediately extinguished.\* This shows that nitric oxide does not support combustion. The same happens if feebly burning phosphorus is plunged into the gas. Intensely burning phosphorus, however, decomposes nitric oxide, and burns in it almost as brilliantly as in oxygen itself. The cause for its burning less brilliantly is evidently the presence of the inert nitrogen, which fixes much of the heat produced by the combination of the phosphorus with the oxygen. This nitrogen acts as a heat diluent. Temperature as well as pressure influences the amount of light given off by burning bodies.

Nitric oxide has never been liquefied. Its vapour density is anomalous, since its molecule occupies four volumes instead of two. This is known to be the case with a few other bodies alike irregular in their vapour density. One volume of this gas dissolves in about twenty of water at 15° C. Its specific gravity compared with air is 1.039.

Other metals, *e.g.*, lead and mercury, are acted upon by nitric acid in like manner, *i.e.*, they are converted into nitrates.



Others again, deoxidize nitric acid to a less extent, such as tin and silver—

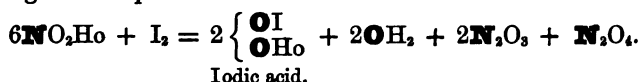


In this latter reaction, however, the colourless gas  $\text{ON}_2$ , called *nitrous oxide* (also known as *laughing gas*), is never free from the higher oxides,  $\text{N}_2\text{O}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ ; and the reaction is not nearly so perfect as that which took place when copper was acted upon by nitric acid. We may then sum up by saying, *that ruddy vapours result from the action of nitric acid upon metals.*

Nitric acid oxidizes likewise most of the metalloids with evolution of red fumes. Powdered charcoal, when treated with nitric acid at a high temperature, decomposes it entirely with formation of carbonic anhydride and nitrogen. A mixture of finely powdered nitre and charcoal deflagrates violently (small quantities only should be mixed), potassic carbonate being left. Sulphur is gradually oxi-

\* Nitric oxide prepared from copper and nitric acid sometimes contains so much nitrous oxide, that a taper burns in it brilliantly.

dized into sulphuric acid; metallic sulphides into sulphates. Phosphorus is oxidized into phosphoric acid. Dilute nitric acid (sp. gr. 1.20) should be employed, and small pieces of phosphorus only should be introduced into the hot acid at a time. By employing amorphous or red phosphorus, the danger of an explosion is avoided. Iodine is oxidized by strong boiling nitric acid into iodic acid, according to the equation:—



Wood, wool, horn, skin, silk, are stained yellow by dilute acid, and are converted by concentrated nitric acid into compounds of great practical importance, such as oxalic acid, gun-cotton, etc.

The five compounds which nitrogen is capable of forming with oxygen illustrate very well the law of constant combining proportions, according to weight and volume, as will be seen from the following table:—

	By volume.	By weight.
Nitrous oxide . . . . $\text{ON}_2$	2 vols. of N, and 1 vol. of O	28 + 16 = 44.
Nitric oxide . . . . . $\text{N}_2\text{O}_2$	2 vols. of N, and 2 vols. of O	28 + 32 = 60.
Nitrous anhydride $\text{N}_2\text{O}_3$	2 vols. of N, and 3 vols. of O	28 + 48 = 76.
Nitric peroxide . . $\text{N}_2\text{O}_4$	2 vols. of N, and 4 vols. of O	28 + 64 = 92.
Nitric anhydride . . $\text{N}_2\text{O}_5$	2 vols. of N, and 5 vols. of O	28 + 80 = 108.

We must content ourselves with merely referring in a tabular form to the molecular composition of these five bodies; remarking that nitric oxide and nitric peroxide show anomalous molecular volumes—

	Molecular weight.	Molecular volume.	Specific gravity referred to hydrogen.
Nitrous oxide . . . . $\text{ON}_2$	44	2 vols. ....	<input type="text"/> <input type="text"/> 22 criths.
Nitric oxide . . . . . $\text{N}_2\text{O}_2$	60	4 vols. ....	<input type="text"/> <input type="text"/> 15 "
Nitrous anhydride . . $\text{N}_2\text{O}_3$	76*	2 vols.*....	<input type="text"/> <input type="text"/> 38 "
Nitric peroxide . . { $\text{N}_2\text{O}_4$ 46	{ 2 vols. at 0° C. to 92	{ to 4 vols. at 100° C. }	<input type="text"/> <input type="text"/> 23 to 46 criths.
Nitric anhydride . . $\text{N}_2\text{O}_5$	108*	2 vols.*....	<input type="text"/> <input type="text"/> 54 criths.

\* These molecular combinations have not been determined with absolute certainty, and the above figures represent merely their probable composition.

All the preceding experiments have shown that we possess in nitric acid (sometimes called *aqua fortis*) a powerful solvent for metals. This is owing to the mobile nature of three out of the five oxygen atoms contained in each molecule; hence the slight resistance which the acid offers to the deoxidizing action of the elements, especially metals, whereby the nitric acid is partially or entirely deprived of its oxygen. Gold and platinum are not affected, *i.e.*, not oxidized either by nitric or hydrochloric acid when in an unalloyed condition.

Aluminium strongly resists the action of nitric acid, even at a boiling heat.

Tin and antimony are converted into oxides, insoluble in nitric acid. Concentrated nitric acid does not act upon iron and tin at the ordinary temperature, though it dissolves them rapidly when diluted. When iron is immersed in concentrated nitric acid (sp. gr. 1.45), it remains unacted upon; and when subsequently placed in dilute acid, without first being wiped, it cannot be dissolved; it is said to assume the *passive* state. The cause of this peculiar action has not yet been satisfactorily explained.

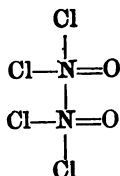
Comparatively few of the nitrates are commonly met with; the most important are—

Potassic nitrate ( <i>nitre, saltpetre</i> ) .....	$\text{NO}_2\text{Ko.}$
Sodic nitrate ( <i>cubic nitre, or Chili saltpetre</i> ) .....	$\text{NO}_2\text{NaO.}$
Baric nitrate.....	$\text{NO}_2\text{BaO''.}$
Strontic nitrate .....	$\text{NO}_2\text{SrO''.}$
Cobaltous nitrate.....	$\text{NO}_2\text{CoO''.}$
Plumbic nitrate .....	$\text{NO}_2\text{PbO''.}$
Bismuthous nitrate.....	$\text{NO}_2\text{Bio'''}$
Argentive nitrate ( <i>lunar caustic</i> ).....	$\text{NO}_2\text{AgO.}$
Mercuric nitrate .....	$\text{NO}_2\text{HgO''.}$

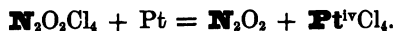
A mixture of six molecules of hydrochloric, and two molecules of nitric acid, is called *aqua regia* or *nitro-hydrochloric acid*—



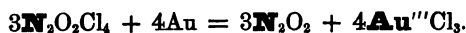
The compound  $\text{N}_2\text{O}_2\text{Cl}_4$  *chloronitric gas*, graphic formula—



may be viewed as nitric peroxide, in which two atoms of dyad oxygen are replaced by four atoms of monad chlorine.  $\text{N}_2\text{O}_2\text{Cl}_4$  is of a still more unstable nature than the compound  $\text{N}_2\text{O}_4$ . It forms a readily available source of chlorine, and is employed for dissolving gold and platinum, since chlorine acts in the nascent state on these metals, and forms with them soluble chlorides—



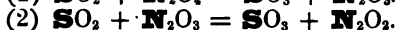
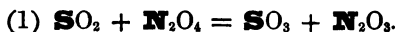
Platinic  
chloride.



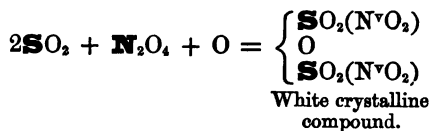
Auric chloride.

Nitric oxide on escaping into the air, gives rise to the well-known ruddy fumes; and aqua regia ought to be used only where there is a good draught to carry off these fumes.

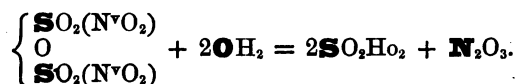
The gas which results from the action of nitric acid or aqua regia upon metals, escapes and partially recovers from the air the oxygen which the nitric acid gave up to the metals. Its tendency is to combine with two atoms of oxygen, and no more; and this oxygen it yields up again quite as readily to other bodies that have a stronger affinity for that element than either nitrous anhydride or nitric peroxide possesses. Upon this remarkable property of nitric oxide is based one of the most beautiful chemical processes, viz., the manufacture of oil of vitriol or sulphuric acid. We have seen that sulphur when burned in air combines never with more than two atoms of oxygen to form sulphurous anhydride. Here, then, is a body that wants one more atom of oxygen in order to be converted into sulphuric anhydride,  $\text{SO}_3$ : and in the  $\text{N}_2\text{O}_4$  we have a body that can readily part with one or two atoms of oxygen. Hence sulphuric anhydride results from the reaction of these two bodies, according to the equations—



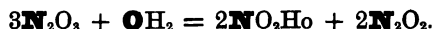
If we add to these two conditions two others, viz., a well regulated supply of steam (to form sulphuric hydrate) and atmospheric air, or some other source of oxygen (to reoxidize the  $\text{N}_2\text{O}_2$  as fast as it is formed), the conversion of sulphurous into sulphuric acid becomes a *continuous* process. A peculiar white compound which is first formed is only a transitory product, and has little interest attached to it—



The water or steam decomposes it in its turn—



Nitrous anhydride we have already seen, cannot exist in the presence of water. It is at once broken up into nitric oxide and nitric acid—



Nitric oxide, in the presence of air, is converted into nitric peroxide. The nitric acid and nitric peroxide thus formed, can, in their turn, oxidize fresh quantities of sulphurous anhydride. By the proper supply of sulphurous anhydride, steam, air, and nitric oxide, which acts as a *carrier* of oxygen, a continuous process of manufacture of this important substance—sulphuric acid—can be readily secured.

These interesting reactions may also be studied on an experimental scale.

**Experiment 120.**—Fig. 64 represents a tall wide glass cylinder fitted with an india-rubber cork and five glass tubes, and connected with apparatus for generating steam, sulphurous anhydride, oxygen, and  $\text{N}_2\text{O}_2$ . The two latter gases may also be stored up and conveyed to the cylinder directly from gas-holders. The unappropriated tube communicates with the air. As soon as the first few bubbles of nitric oxide are admitted into the cylinder dense ruddy fumes of  $\text{N}_2\text{O}_4$  are seen, which disappear on the admission of the sulphurous anhydride. The contents of the globe become colourless, and the white crystals described above make their appearance on the sides of the glass. If a slow current of oxygen be now admitted the red fumes reappear immediately, only to be decolourised again, however, according as the current of sulphurous anhydride is regulated. The white crystals which have become more numerous disappear as soon as steam is admitted to the cylinder. By properly regulating the admission of  $\text{N}_2\text{O}_2$ , oxygen,  $\text{SO}_2$ , and steam, the process becomes continuous.

Now substitute for the glass cylinder the ordinary lead chambers used by the manufacturer of sulphuric acid, and for the oxygen air; generate the sulphurous anhydride either by burning sulphur, or, as is done more frequently now, by roasting iron pyrites,  $\text{Fe}^\vee\text{S}_2$ , in a current of air, and decompose sodic nitrate or Chili saltpetre by means of oil of vitriol, and we have the outlines of the manufacturing process as it is now carried on.

The sulphuric acid thus obtained—so-called *chamber acid*, of sp. gr. 1·6, containing 70 p. c. of oil of vitriol, is quite strong



FIG. 64.—PREPARATION OF SULPHURIC ACID.

enough to be used for decomposing sodic chloride into sodic sulphate, preparatory to the conversion of the latter into sodic carbonate. Evaporation in leaden pans brings the specific gravity up to 1.72, and the acid contains then about 80 p. c. of oil of vitriol. It is technically known as *brown acid*, and is largely used for making superphosphates, etc. Further concentration and purification of this acid is carried on in glass vessels, or more frequently now in platinum stills. The specific gravity of the concentrated acid is 1.842. It is free from odour, and forms an oily highly corrosive liquid, which boils at about 338°, and solidifies when cooled to -10.8°. It attracts moisture from the air, and may therefore be used for drying gases which are not acted upon by the acid, *e.g.*, N, O, H, Cl, etc.

The following is a list of some of the most important metallic sulphates:—

Potassic sulphate.....	$\text{SO}_2\text{Ko}_2$
Sodic sulphate ( <i>Glauber's salt</i> ).....	$\text{SO}_2\text{NaO}_2 + 10\text{OH}_2$
Hydric potassic sulphate .....	$\text{SO}_2\text{HoKo}$
Ammonic sulphate .....	$\text{SO}_2\text{Amo}_2$
Baric sulphate ( <i>heavy spar</i> ) .....	$\text{SO}_2\text{Bao''}$
Strontic sulphate ( <i>celestine</i> ) .....	$\text{SO}_2\text{Sro''}$
Calcic sulphate ( <i>gypsum</i> ) .....	$\text{SHo}_4\text{Cao''}$
„ ( <i>anhydrite</i> ) .....	$\text{SO}_2\text{Cao''}$
Magnesian sulphate ( <i>Epsom salts</i> ) .....	$\text{SO}_2\text{Mgo''} + 7\text{OH}_2$
Aluminic sulphate .....	$\text{SO}_2\text{Al}_2\text{O}^{\text{VI}}$
Potash alum.....	$\text{SO}_2\text{Al}_2\text{O}^{\text{VI}} + 24\text{OH}_2$
Chrome alum .....	$\text{SO}_2\text{Cr}_2\text{O}^{\text{VI}} + 24\text{OH}_2$
Ferrous sulphate ( <i>green vitriol</i> ) .....	$\text{SO}_2\text{Feo''} + 7\text{OH}_2$
Ferric sulphate .....	$\text{SO}_2\text{Fe}_2\text{O}^{\text{VI}} + 9\text{OH}_2$
Cobaltous sulphate .....	$\text{SO}_2\text{Coo''}$
Nickelous ( <i>sulphate</i> ) .....	$\text{SO}_2\text{Nio''} + 7\text{OH}_2$
Manganous sulphate .....	$\text{SO}_2\text{Mno''} + 5\text{OH}_2$
Zincic sulphate ( <i>white vitriol</i> ) .....	$\text{SO}_2\text{Zno''} + 7\text{OH}_2$
Plumbic sulphate .....	$\text{SO}_2\text{Pbo''}$
Cupric sulphate ( <i>blue vitriol</i> , or <i>blue stone</i> ) .....	$\text{SO}_2\text{Cuo''} + 5\text{OH}_2$
Mercuric sulphate.....	$\text{SO}_2\text{Hgo''}$
Basic mercuric sulphate ( <i>turpeth mineral</i> ).....	$\text{SHgo''}_2\text{Hgo''}$
Argentio sulphate.....	$\text{SO}_2\text{Ago}_2$

## QUESTIONS AND EXERCISES.

1. Mention some natural saline compounds in which nitrogen occurs.
  2. Describe a process for preparing small quantities of nitric acid by the *direct* combination of nitrogen and oxygen.
  3. Explain the formation of saltpetre in tropical countries.
  4. You have given to you Chili saltpetre and sulphuric acid. Describe how you would prepare nitric acid from these materials. Express the chemical change by an equation.
  5. Calculate how much nitric acid ( $\text{HNO}_3$ ) by weight can be obtained from 20 grms. of potash nitre; and how much sulphuric acid ( $\text{H}_2\text{SO}_4$ ) by weight is required in order to have only dipotassic sulphate left in the retort.
  6. Show why you write  $\text{HNO}_3$ , and not  $\text{NO}_3\text{H}$ .
  7. Give symbolic and graphic formulæ for nitric anhydride and nitric acid.
  8. State how metallic nitrates are prepared. Give equations.
  9. You have given to you a few iron nails, some pure tin foil, copper filings, and a little granulated zinc, with concentrated nitric acid and distilled water. State what chemical changes you can produce with these materials, and express the changes by equations.
  10. Explain what takes place when cupric or bismuthous nitrate is heated in a retort.
  11. What takes place when the vapour of  $\text{N}_2\text{O}_4$  is passed into a solution of baric hydrate? Express the changes by equations.
  12. How is nitrous anhydride prepared?
  13. Explain the reducing and oxidizing action of nitrous anhydride, or of nitrites, in the presence of an acid.
  14. Give symbolic and graphic formulæ for nitric peroxide, nitrous anhydride, nitrous oxide, argentic nitrite.
  15. Describe the properties of nitric oxide gas.
  16. Explain the action of concentrated nitric acid upon mercury and silver, sulphur, phosphorus, and iodine. Express the changes by equations.
  17. Commit to memory the list of all the oxides of nitrogen, together with their atomic and volume weights.
  18. Explain the terms *aqua fortis*, *aqua regia*, *cubic nitre*, *lunar caustic*, *chamber acid*, *ignition point*.
  19. Explain the action of aqua regia upon gold and platinum.
  20. Explain the important use of some of the nitrogen oxides in the manufacture of oil of vitriol.
  21. Calculate the percentage composition of potassic nitrate.
  22. How much argentic nitrate can be prepared from ten ounces of metallic silver?
  23. What evidence have you to adduce that nitrogen occurs as a pentad, as a triad, and as a monad element?
  24. Practise writing out the graphic formulæ of some of the most important nitrates and sulphates.
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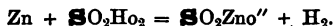
## CHAPTER XVII.

## AMMONIA.

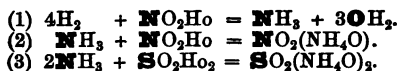
FREE hydrogen and nitrogen possess very little affinity for one another, so that they cannot be united directly. A terhydride of nitrogen (three atoms of hydrogen and one atom of nitrogen) called *ammonia*,  $\text{NH}_3$ , is known. This is for the most part derived from the nitrogen contained in nitrogenous organic substances, such as coal, hair, horn (whence its ordinary name of *spirit of hartshorn*), skin, sinews, etc. The greater part of the animal body (fat excepted) consists of organic substances rich in nitrogen; and they all yield, under certain conditions (dry distillation, putrefaction, etc.), the pungent gas called *ammonia*.

**Experiment 121.**—Rub together in a mortar a mixture of pulverized unslaked lime and caustic soda (called soda-lime) with some animal substance, such as glue, white of egg, horn shavings; then introduce the mixture into a test-tube, and apply heat. A pungent gas is given off, which turns red litmus-paper blue, and yields white fumes when a glass rod moistened with dilute hydrochloric acid is held in the gas.

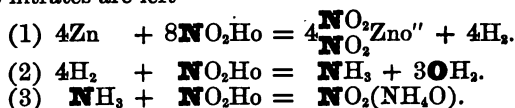
**Experiment 122.**—Treat a little zinc with dilute sulphuric acid; hydrogen gas is evolved—



Add now, drop by drop, dilute nitric acid. The evolution of gas ceases, but the zinc nevertheless disappears. The hydrogen combines with the elements of nitric acid to form water and ammonia, which latter immediately enters into combination with the acids:—



A similar reaction takes place when zinc is dissolved in moderately dilute nitric acid. Owing to a secondary reaction, hydrogen and nitrogen combine to form ammonia, and zincic and ammoniac nitrates are left—



The action of nitric acid upon zinc is invariably accompanied by the formation of lower oxides of nitrogen,  $\text{ON}_2$ ,  $\text{N}_2\text{O}_2$ , etc., which offer little resistance to the action of the hydrogen, and yield under favourable circumstances nitrogen and water. Nitrogen and hydrogen, when together in the nascent state, *i.e.*, at the very moment\* of their liberation, combine and form ammonia,  $\text{NH}_3$ . The solution contains a considerable amount of ammoniac nitrate, which may be proved by heating some of it with a little soda-lime.

\* The elements may be supposed to exist for a moment in the uncombined state.

**Experiment 123.**—Prepare some ammoniac nitrate by neutralizing a solution of ammonia or ammoniac carbonate with dilute nitric acid (comp. Exp. 44). Evaporate the solution of the salt to dryness and fuse the crystals gently in a porcelain dish on a sand-bath. Pour out the fused mass on an iron plate, and reduce it when cold to a coarse powder.

**Experiment 124.**—Heat some of the coarsely powdered ammoniac nitrate in a Florence flask, provided with a delivery-tube, or in a small retort (Fig. 65). The salt melts, boils, and gradually breaks up into nitrous oxide (or laughing gas),  $\text{ON}_2$ , and steam. The gas may be collected over water.

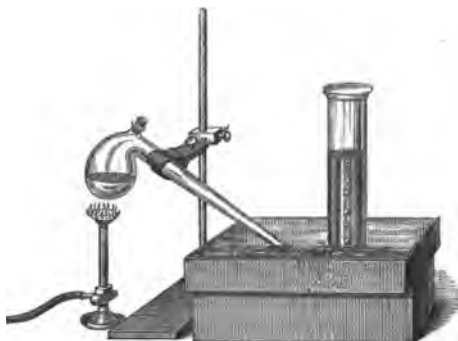
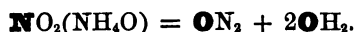


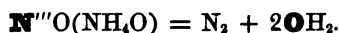
FIG. 65.—PREPARATION OF NITROUS OXIDE.

The decomposition of ammoniac nitrate takes place, according to the equation:—



Nitrous oxide is a colourless gas, with a slight smell and a sweetish taste. Its specific gravity, compared with air, is 1.527; its volume weight ( $\text{H} = 1$ ) is 22. One litre of nitrous oxide weighs  $22 \times .0896 \text{ grm.} = 1.9712 \text{ grm.}$  Nitrous oxide, when mixed with air, undergoes no change. Water absorbs it to a certain extent (1.3 of its volume at  $0^\circ \text{C.}$ ). This solubility distinguishes the gas readily from oxygen. A glowing piece of charcoal, when introduced into the gas, burns almost as brilliantly as we saw carbon burn in oxygen (comp. Exp. 24). A glowing splinter of wood bursts into flame, and burns brilliantly in the gas. A piece of sulphur placed in a deflagrating spoon and introduced into the gas immediately after kindling and whilst it burns only feebly, is extinguished. Introduce it when burning briskly and it will burn with increased brilliancy almost as if in oxygen itself, with a pale rose-coloured flame. Atmospheric air, we know, sustains respiration. Certain animals are able to breathe nitrous oxide (which we may view as an air considerably richer in oxygen—36.4 p. c.) with impunity for several hours. When inhaled by man, it produces a characteristic kind of exhilarating intoxication, which is sometimes accompanied by immoderate laughter; hence its name *laughing gas*. Pure gas only should be employed for purposes of inhalation. Nitrous oxide has of late been recommended as an *anæsthetic*, or agent for suspending the mental and sensorial functions during dental and surgical operations.

Ammoniac nitrite heated in like manner yields nitrogen and water, according to the equation—



**Experiment 125.**—Heat gently a concentrated aqueous solution of potassic nitrite and ammonic chloride in a retort (comp. Fig. 65). The nitrite decomposes at about 50° C. into nitrogen gas, which can be collected over water, potassic chloride, and water, according to the equations—



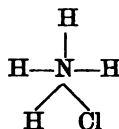
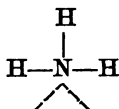
Test the gas with a burning taper. The light is immediately extinguished.

**Experiment 126.**—Fill a glass cylinder with ammonia gas, by rinsing it out with a few drops of strong solution of ammonia (the *liquor ammonia* of the shops); cover it with a glass plate. Another cylinder or bottle is filled with hydrochloric acid gas. The two bottles or cylinders are then placed together (as seen in Fig. 43), and the glass plates withdrawn, so that the mouth of the inverted vessel containing the hydrochloric acid gas rests almost air-tight on the mouth of the lower vessel. Both gases are seen to mix, and to combine, producing clouds of white fumes.

These clouds are deposited on the sides of the glass vessels as a white salt, called ammonic chloride (*sal-ammoniac*), a compound of the ammonia and hydrochloric acid gas—



The nitrogen atom in  $\text{N}^{\text{III}}\text{H}_3$  is combined only with three atoms of hydrogen, and is therefore triadic; but it is also clear from the avidity with which  $\text{N}^{\text{III}}\text{H}_3$  combines with  $\text{HCl}$ , that two more affinities remain *latent*, one of which can become satisfied by hydrogen, the other by chlorine, thus:—

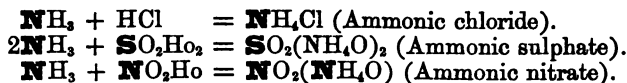


**Experiment 127.**—Heat gently in a test-tube a concentrated solution of ammonic chloride in water, with sodic or potassic hydrate. Colourless ammonia gas is evolved, according to the equation—

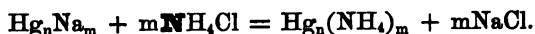


and is readily recognised, 1st, by its characteristic pungent odour; 2nd, by its action upon red litmus-paper or turmeric-paper (changed from red to blue, and from yellow to brown); and 3rd, by the white clouds which it produces when a glass rod, moistened with dilute hydrochloric, sulphuric, or nitric acid is held at the mouth of the test-tube.

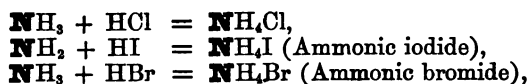
Ammonia forms with these acids the respective salts—



The compound  $\text{NH}_4$  appears to be capable of existing only as an amalgam. It is obtained by mixing sodium-amalgam ( $\text{Hg}_n\text{Na}_m$ ) with a concentrated solution of ammonic chloride—



Sodium exerts its well known affinity for chlorine, forming with it sodic chloride; the amalgam breaks up very rapidly into  $2n\text{Hg}$ ,  $2m\text{NH}_3$ , and  $m\text{H}_2$ , which is evolved. On account of its salts possessing a marked similarity to potassic and sodic salts, the existence of a hypothetical metal ammonium,  $\text{NH}_4$ , has been entertained by chemists. Ammonium is affected like the alkali metals, potassium and sodium. Its haloid salts,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{I}$ ,  $\text{NH}_4\text{Br}$ , which are well defined salts, can therefore also be viewed as derived from



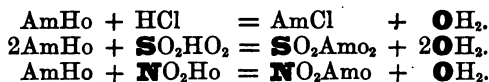
by assuming that the atom hydrogen attacks the molecule  $\text{NH}_3$  first, forming with it  $\text{NH}_4$ , or the hypothetical metal called—in accordance with the terminology adopted by chemists—*Ammonium*. Since this metal combines with one atom of chlorine, it must be viewed as a monad, like potassium or sodium; and as it consists of one atom of nitrogen, and four atoms of hydrogen, and yet acts the part of an element, it is called a compound radical. It is usually written *Am*, instead of  $\text{NH}_4$ , forming ammonoxyl, *Amo*, analogous to the radicals *Ho*, *Ko*, etc.

Ammonic hydrate formed, according to the equation—



appears likewise to have only a hypothetical existence, as no chemical combination seems to take place between the water and the ammonia; for the gas gradually escapes on exposing the solution to the air, and no definite compound of ammonia and water has been observed. The escape of the gas from the solution is marked by the production of intense cold: *i.e.*, much heat becomes latent, when ammonia passes from the liquid to the gaseous state. This property has found a practical application for refrigerating purposes, and for producing ice artificially.

Ammonic chloride, sulphate, or nitrate, are best obtained by the action of the respective acids upon the ammonic hydrate:—



**Experiment 128.**—Heat a little sal-ammoniac in an iron spoon, or on platinum foil. White fumes are given off. When the salt is heated in a test-tube, the fumes condense in the upper or colder part of the tube; the salt *sublimes* unchanged.

Most salts of ammonium *volatilize* upon the application of heat.

This property renders ammonic salts of great value in chemical analysis.

A solution of ammonia gas in water is indispensable in the laboratory. It is therefore important to study its preparation and properties.

**Experiment 129.**—Ammonia gas is very soluble in water. This may be shown by heating a little strong ammonia in a small flask (Fig. 66) and passing the evolved gas over freshly burnt lumps of lime,\* placed in a wide U-tube.

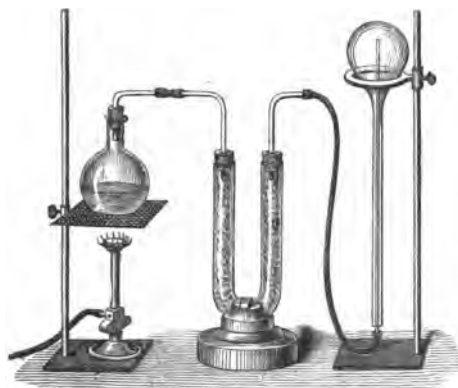


FIG. 66.—COLLECTION OF DRY AMMONIA GAS AND ABSORPTION BY WATER.

Any moisture which the ammonia gas carries with it is retained by the lime. From the drying tube the gas is passed into an inverted long-necked glass globe, which should be well dried first, and is collected by upward displacement. When full, the globe is closed with the thumb, and is plunged, with its mouth downwards, into a bowl of water, reddened with a solution of litmus and a few drops of sulphuric acid. By cautiously withdrawing the thumb under water, the latter rushes in most eagerly, and fills the whole globe almost instantaneously. The liquid which is left in the flask reacts alkaline, for the solution is turned blue.

Water absorbs about 700 times its bulk of the gas.

**Experiment 130.**—A concentrated solution of ammonia is obtained by distilling in a flask a mixture of sal-ammoniac and calcic hydrate. The gas is made to pass through a wash-bottle, containing a little water, and from thence through one or more Woulfe's bottles, filled about three-fourths with water (as shown in Fig. 47). No funnel-tube is, however, required. The delivery-tubes must reach nearly to the bottom, as aqueous ammonia is lighter than water. The specific gravity of the solution diminishes, therefore, in proportion as the water becomes saturated with the gas. The liquid also increases in bulk, and when saturated at 15° C., it contains more than a third of its weight of the alkali.

Dry ammonia gas may be collected by displacement (imperfectly), or over mercury.

**Experiment 131.**—Collect some ammonia gas by displacement, and plunge a lighted taper into the inverted cylinder (comp. Fig. 8). The flame becomes first slightly enlarged and then extinguished. The enlargement is due to a very slight and evanescent combustion of the gas. During its combustion, the hydrogen combines with the atmospheric oxygen, and is converted into water, and the nitrogen is set free. The igniting point of ammonia, like that of nitrogen, being higher than the temperature produced by its combustion, the flame becomes extinguished.

**Experiment 132.**—Pass a current of ammonia gas through a porcelain-tube placed in a Hofmann's combustion furnace, and fitted with a delivery-tube

---

\* Calcic chloride cannot be used, because it absorbs a considerable quantity of the gas; nor oil of vitriol, because ammonia combines with the acid with explosive violence.

drawn out to a fine jet. Apply a light to the gas as it issues from the jet. The gas will not burn readily, but a pale greenish flame will play over the top of the light. By gradually heating the tube in the gas furnace, and thus raising the initial temperature of the gas, it may be made to burn. On slowly cooling the tube by turning off the gas, the flame will go out again.

By substituting, however, oxygen for air, by mixing the two gases in a Hemming's jet used for the combustion of hydrogen and oxygen—the so-called oxy-hydrogen blowpipe—the gas may be made to burn readily with a greenish yellow flame.

**Experiment 133.**—Heat the porcelain-tube used in Exp. 132 red hot. The issuing gas burns now readily in the air, but is no longer ammonia; the heat has decomposed it into hydrogen, which burns, and nitrogen. This may be shown by passing the gas into water acidulated with a little acid, in order to absorb any undecomposed ammonia, and collecting over a pneumatic trough. The gas so collected consists of a mixture of 1 vol. of nitrogen and 3 vols. of hydrogen.

**Experiment 134.**—Pass some well-dried ammonia-gas over some small pieces of potassium (sodium) placed in a bulb-tube made of hard glass (Fig. 67),



FIG. 67.—DECOMPOSITION OF AMMONIA BY SODIUM.

and heat the bulb gently by means of a small gas flame. The metal potassium displaces a part of the hydrogen, and forms a compound having the composition  $\text{NKH}_2$  (potassamine). The issuing gas burns readily; it has all the properties of hydrogen.

The composition by volume and by weight of ammonia gas has been carefully determined.

Its volumetrical composition cannot, however, be demonstrated so readily, as, for instance, that of steam or hydrochloric acid gas. Ammonia is decomposed by bringing it into contact with chlorine; and for every three volumes of chlorine so employed, one volume of nitrogen is left. The hydrochloric acid, resulting from the combination of hydrogen and chlorine, combines with the excess of ammonia, and forms the solid salt,  $\text{NH}_4\text{Cl}$ . This reaction is sometimes employed for preparing pure nitrogen.

caution is, however, necessary, on account of the possible formation of highly explosive chloride of nitrogen. The ammonia solution used should be concentrated, and always in large excess, and the delivery-tube should be wide, on account of the formation of solid ammoniac chloride.

By passing electric sparks for some time through dry ammonia gas, placed in a eudiometer-tube over mercury, the gas is slowly decomposed into its component elements, hydrogen and nitrogen. The gas volume is seen to increase gradually, till the original volume has been doubled. The four volumes of mixed gases are found on analysis to consist of three volumes of hydrogen and one volume of nitrogen; and one volume of ammonia gas is derived from  $1\frac{1}{2}$  volumes of hydrogen and  $\frac{1}{2}$  of nitrogen, weighing respectively  $\cdot 1036$  and  $\cdot 4856$ , total =  $\cdot 5892$  (sp. gr. of H =  $\cdot 0691$ , and of N =  $\cdot 9712$ , when compared with air).

Direct estimation of the specific gravity of ammonia gas (compared with air) gave the number  $\cdot 597$ , from which the above differs but little.

The percentage composition is readily found by rule of three calculation, viz. :—

Hydrogen .....	17.61
Nitrogen .....	82.39

The molecular weight of  $\text{NH}_3$  is 17. The specific gravity of ammonia gas compared with hydrogen is therefore 8.5, and one litre of ammonia gas weighs  $\frac{1}{2} \times 8.5 = 8.5 \times \cdot 0896 \text{ grm.} = \cdot 7616 \text{ grm.}$

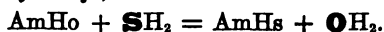
Gaseous ammonia can be liquefied by cooling it down to  $-40^\circ \text{C.}$ , or by a pressure of 7 atmospheres at  $15^\circ \text{C.}$  It may even be frozen by exposing the dry gas to a pressure of 20 atmospheres, and to a cold of  $-75^\circ \text{C.}$  It forms then a white, transparent, crystalline body.

Ammonia neutralizes the most powerful acids, forming with them salts which are readily volatilized by heat, unless they contain non-volatile acids, when the ammonia only is driven off.

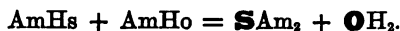
A few compounds of ammonia briefly claim our attention, as they constitute some of our most important reagents.

**Experiment 135.**—Measure out two equal portions of a solution of ammonia or ammoniac hydrate, also called simply ammonia. Pass through one portion a brisk current of sulphuretted hydrogen gas, as long as the gas continues to be absorbed. (The apparatus described for the preparation of chlorine water answers admirably.) Then add the second portion to it, and a solution of ammoniac sulphide,  $\text{SAm}_2$ , is obtained.

By completely saturating a solution of ammonia with sulphuretted hydrogen, we obtain a solution of hydric ammoniac sulphide,  $\text{AmHs}$ , in which the compound radical hydrosulphyl,  $\text{Hs}$ , has taken the place of the hydroxyl, thus :—



On then adding  $\text{AmHo}$  to this solution, ammoniac sulphide is obtained, thus :—



**Experiment 136.**—Fill a cylinder with dry carbonic anhydride gas, and another cylinder of double the size with dry ammonia gas. On bringing the mouths of the two cylinders towards each other, the two gases rush together, and form the compound  $2\text{NH}_3\text{CO}_2$ . This body attracts moisture rapidly, and dissolves to a salt having the composition  $\text{COAmo}_2$ , ammonic carbonate.

**Experiment 137.**—Pass a current of  $\text{CO}_2$  through a concentrated solution of ammonia as long as any gas is absorbed. On setting the solution aside for crystallisation beautiful colourless rhombic prisms are obtained, which have the composition  $\text{COHoAmo}$  (hydric ammonic carbonate).

Notice the smell of the crystals.

Solutions of both these ammonium compounds are employed in the laboratory.

#### QUESTIONS AND EXERCISES.

1. Which are the chief sources whence ammonia and its compounds are derived?
2. You have given to you some glue and soda-lime. Show how you would prepare  $\text{NH}_3$  from these materials.
3. Explain the formation of ammonia by the aid of dilute sulphuric acid, metallic zinc, and dilute nitric acid. Express the changes by equations.
4. How would you prepare, 1st, ammonic nitrate, and 2nd, nitrous oxide gas?
5. What are the properties of nitrous oxide?
6. You have given to you 25 grms. of pure ammonic nitrate. How much laughing-gas, by weight and by volume, can you prepare from it?
7. Write out the symbolic and graphic formulæ for ammonia, ammonic bromide, carbonate, hydric ammonic sulphide, ammonic nitrate, and nitrite.
8. Explain the terms *nascent state*, *sal-ammoniac*, *spirit of hartshorn*.
9. Describe the formation of ammonium-amalgam, and give reasons why the group of elements,  $\text{NH}_4$ , is considered to be a metal.
10. Why are  $\text{NH}_4$  and  $\text{AmHo}$  considered hypothetical compounds?
11. How would you show experimentally that most ammonium compounds can be volatilized and sublimed?
12. What space will 5.324 grms. of ammonia gas occupy at  $15^\circ \text{C}$ ., and 745 mm. barometric pressure?
13. How are neutral ammonic sulphide and hydric ammonic carbonate prepared?
14. How would you prepare and collect dry ammonia gas?
15. How is a concentrated solution of ammonia in water (*liquor ammonia*) prepared?
16. Describe several methods of preparing pure nitrogen. Give equations.
17. Explain the decomposition of  $\text{NH}_3$  by heat and by sodium. Give equations.

#### CHAPTER XVIII.

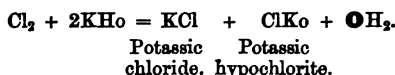
#### OXIDES OF CHLORINE. CHLORATES. HYPOCHLORITES.

CHLORINE has but little affinity for oxygen. No method is known by which it can be made to unite directly with this element, and the compounds which can be formed by indirect means are mostly of a very unstable nature. Heat alone breaks them up readily, often with explosive violence. Only two of the oxygen compounds

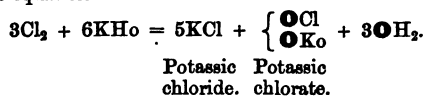


of chlorine, viz., the salts known as *chlorates* and *hypochlorites*, are of practical importance.

**Experiment 138.**—Pass a current of chlorine gas slowly into a solution of potassic hydrate,  $\text{KHO}$ . If the solution be dilute and kept cool by a current of cold water, the reaction takes place according to the equation :—



If concentrated (one of  $\text{KHO}$  to three of water) and kept at boiling-water temperature, chlorine is rapidly absorbed, and the change which takes place is expressed by the equation :—



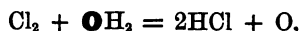
The two salts are readily separated by crystallisation : potassic chlorate, being sparingly soluble, crystallises out in plates, which can be obtained pure by recrystallisation.

We have seen that chlorine breaks up water under the influence of sunlight (Exp. 62), or steam under that of heat (Exp. 63). If instead of water we employ potassic hydrate, i.e., water in which one atom of hydrogen has been replaced by the metal potassium, the oxygen instead of being given off, attaches itself to a portion of the potassic chloride which is formed; the quantity of oxygen which is thus fixed varies with the temperature at which the chemical change takes place.

In the first reaction a liquid is obtained containing the salt called potassic *hypochlorite*, which possesses powerful bleaching and disinfecting properties. It yields its oxygen again readily. Dilute hydrochloric acid evolves chlorine, both from the hypochlorite and from the acid itself, thus :—

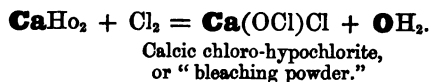


The chlorine by decomposing water liberates oxygen, thus :—



or by combining with the hydrogen of organic substances and taking the place of this element, acts directly or indirectly as a bleaching agent.

The best known hypochlorite is the so-called *bleaching powder* or *chloride of lime*. It is prepared on a very large scale for the purposes of bleaching cotton goods, by passing chlorine gas over layers of slaked lime placed in large chambers, the so-called chlorine chambers. The reaction appears to take place according to the equation—



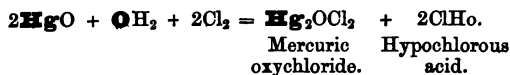
Bleaching powder undergoes a slow decomposition even at the ordinary temperature, giving off oxygen and leaving calcic chloride. Instances are known of glass bottles having been shattered to pieces by the accumulated oxygen; when brought in contact with bodies which have an affinity for oxygen, hypochlorites part readily with oxygen and act thus as powerful *oxidizing agents*.

**Experiment 139.**—Shake up some bleaching powder with a little water and filter. Add some of the solution to a solution of a salt of manganese ( $\text{MnCl}_2$ ), or lead (sugar of lead). A brown precipitate of manganic, or plumbic dioxide is obtained. The bleaching powder parts with its oxygen which combines with the  $\text{MnO}$ , or  $\text{PbO}$ , to form  $\text{Mn}^{\text{IV}}\text{O}_2$ , or  $\text{Pb}^{\text{IV}}\text{O}_2$ , calcic chloride being left in solution.

**Experiment 140.**—Add to a solution of bleaching powder placed in a capacious flask, a few drops of cobaltous chloride,  $\text{CoCl}_2$ , and heat gently. Oxygen is disengaged in large quantities. The cobaltous salt (like the manganous or lead salts in Exp. 139) is immediately oxidized by the bleaching powder, and is converted into cobaltic oxide,  $\text{Co}^{\text{IV}}\text{O}_2$ , and probably into an unstable cobaltic anhydride,  $\text{Co}^{\text{IV}}\text{O}_2$ , which, under the influence of heat, forthwith breaks up into  $\text{Co}^{\text{IV}}\text{O}_2 + \text{O}_2$ , oxygen being given off freely. The cobaltic oxide remains behind when the evolution of oxygen has ceased, and appears to act merely as a carrier of oxygen. Ferric and manganic hydrates produce a similar effect. These two metals are capable of forming acid oxides,  $\text{Fe}^{\text{IV}}\text{O}_2$  and  $\text{Mn}^{\text{IV}}\text{O}_2$ , which part readily with their oxygen. Cupric oxide also acts in an analogous manner, owing probably to the formation of a cupric peroxide,  $\text{Cu}^{\text{IV}}\text{O}_2$ .

**Experiment 141.**—Shake up a solution of bleaching powder (1 in 10 parts of water) with a solution of sodic carbonate (washing-soda) and syphon off or filter. The filtrate contains the sodic hypochlorite, formed by double decomposition, thus:— $\text{Ca}(\text{OCl})\text{Cl} + \text{CONaO}_2 = \text{COCaO}'' + \text{ClNaO} + \text{NaCl}$ , also known by the name of *Eau de Javelle*, and used as a disinfecting fluid, or as a laboratory reagent for purposes of oxidation.

**Experiment 142.**—*Hypochlorous acid*,  $\text{ClHo}$ , can be prepared by passing chlorine gas into water, holding in suspension certain metallic oxides, hydrates, carbonates, etc. Precipitated mercuric oxide or calcic carbonate is practically found to be the most advantageous, thus:—

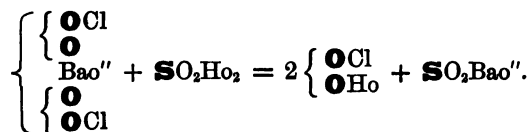


The product of the reaction is rectified by distillation.

Aqueous hypochlorous acid has a yellowish colour, an acrid taste, and a characteristic sweet, chlorine-like smell. The strong acid decomposes rapidly, even when kept in ice. The dilute acid is more stable. It is, like free chlorine, a powerful oxidizing agent.

The corresponding *anhydride*,  $\text{OCl}_2$ , can be prepared by passing the chlorine over dry mercuric oxide, kept cool by ice, or by depriving the hypochlorous acid of its water. It is a yellow gas, which condenses to a blood-red liquid at  $-20^\circ \text{C}$ . It speedily decomposes and explodes from very slight causes, and should not be prepared by beginners, except by taking every possible precaution. The gas may be collected by downward displacement. When passed into water it forms hypochlorous acid:  $\text{OCl}_2 + \text{OH}_2 = 2\text{ClHo}$ .

Chloric acid,  $\left\{ \begin{array}{l} \text{OCl} \\ \text{OHo} \end{array} \right.$ , which enters into the composition of chlorates, is prepared by acting upon baric chlorate by dilute sulphuric acid.



Chloric acid is a colourless, syrupy liquid, having a strong acid reaction. When warmed it gives off a strong, chlorine-like odour. It is somewhat unstable at ordinary temperatures, and undergoes rapid decomposition when heated, being converted into perchloric acid, water, chlorine, and oxygen. It is a very powerful oxidizing and bleaching agent. Dilute acids decompose it with liberation of chlorine. Unlike the hypochlorites and chlorites, the chlorates do not bleach until after the liberation of the acid. Chloric anhydride is not known.

Two intermediate oxides exist, viz., *chlorous anhydride*,  $\text{O}_2\text{Cl}_2$ , and *chloric peroxide*,  $\text{O}_4\text{Cl}_2$ . The former is prepared by acting upon potassic chlorate with nitric acid in the presence of a reducing agent, such as arsenious acid. It is a yellowish-green gas, which is not condensed to a liquid by a cold of  $-20^\circ \text{C}$ . It explodes when heated to  $57^\circ$ , also when brought in contact with sulphur, phosphorus, or arsenic. It should on no account be prepared by beginners. The gas is soluble in  $\frac{1}{5}$ th its volume of water, forming *chlorous acid*,  $\text{OClHo}$ . This acid combines slowly with bases, forming *chlorites*, which are very unstable, and break up easily into chlorates and chlorides.

*Chloric peroxide or chlorine tetroxide* is obtained by the action of sulphuric acid upon potassic chlorate at a low temperature.

**Experiment 143.**—Powder a few crystals of potassic chlorate very finely, and mix with a glass spatula, on a sheet of white paper, with an equal quantity of finely-powdered cane-sugar. Transfer to a brick or tile, and touch it with a glass rod, previously dipped in concentrated sulphuric acid. Chloric peroxide, which is thus set free, causes a vivid combustion of the entire mass.

**Experiment 144.**—Place a few crystals of potassic chlorate at the bottom of a conically shaped glass, filled with water. Add a small piece of phosphorus, and then introduce by means of a pipette drawn out to a fine point, a little concentrated sulphuric acid. As soon as the acid is allowed to come in contact with the salt, chloric peroxide is evolved, which ignites the phosphorus, and gives rise to a vivid combustion.

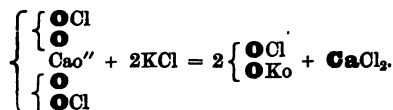
**Experiment 145.**—Put a few crystals of potassic chlorate into a test-tube, and allow a little concentrated sulphuric acid to run down along the sides of the tube. Hold the tube away, with its mouth turned outward, for as soon as the acid comes in contact with the salt, chloric peroxide is given off, and an explosion takes place, which is frequently violent enough to eject some of the contents. By adding the acid to the salt, so as to keep the contents of the tube at a low temperature, a dark greenish gas may be collected by displacement, which, in a diluted form, has a sweetish aromatic odour, and is a powerful oxidizing agent. At  $-20^\circ$  it condenses to an orange-red liquid. On introducing a hot wire into a test-tube containing chloric peroxide, an explosion takes place. The gas explodes with great violence above  $60^\circ$ , often spontaneously.

No corresponding hydrate is known.

There exist still higher oxygenized compounds of chlorine and oxygen, viz., *perchloric acid* and *perchlorates*. The starting point

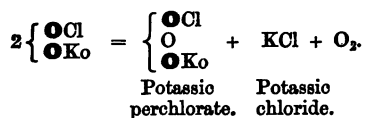
for these bodies is potassic chlorate, a salt which is now largely manufactured and used by lucifer manufacturers, also for detonating powders, pyrotechnical displays, and medicinal purposes.

**Experiment 146.**—Pass a rapid current of chlorine through boiling milk of lime, when calcic chlorate and chloride are formed, analogous to the reaction which takes place when chlorine is passed through a concentrated solution of potassic hydrate. On adding potassic chloride to the solution containing the calcic chlorate, the latter is transformed into potassic chlorate and calcic chloride, thus:—



The potassic chlorate can be more readily separated by recrystallisation from the calcic chloride than from the potassic chloride, owing to the greater solubility of the calcic salt.

When potassic chlorate is heated gradually till about one-third of its oxygen has been evolved, it becomes pasty, and ceases after a time to evolve oxygen. It consists then of a mixture of potassic perchlorate and chloride, thus:—



The two salts are separated by crystallisation, potassic perchlorate being even less soluble than potassic chlorate.

Perchloric acid,  $\text{ClO}_3\text{Ho}$  (no anhydride exists), is obtained from the potassic perchlorate by distilling with about three times its weight of sulphuric acid. A colourless fuming liquid condenses in the receiver, having a specific gravity of 1.78. It does not solidify at  $-35^\circ$ . This acid is a most powerful oxidizing agent; it instantaneously ignites wood or paper, when thrown upon it, and is decomposed with explosion by charcoal. It is the most stable of the chlorine acids. It does not bleach.

TABLE SHOWING THE COMPOUNDS WHICH CHLORINE FORMS WITH OXYGEN, AND WITH OXYGEN AND HYDROXYL.

Names of compounds.	Constitutional formulæ.	Atomic weight.	Molecular weight.	Molecular volume.	Volume weight, or specific gravity referred to hydrogen.
Hypochlorous anhydride. }	$\bullet\text{Cl}_2$	87	87	$\square\square$	43.5 criths
Chlorous anhydride .. }	$\begin{cases} \bullet\text{Cl} \\ \text{O} \\ \bullet\text{Cl} \end{cases}$	119	119	$\square\square\square$ (anomalous)	39.7 "
Chloric peroxide .... }	$\begin{cases} \bullet\text{Cl} \\ \text{O} \\ \text{O} \\ \bullet\text{Cl} \end{cases}$	135	135	?	—
Hypochlorous acid .....	$\bullet\text{ClH}$ or $\text{ClHo}$	52.5	52.5	?	—
Chlorous acid ..	$\bullet\text{ClHo}$ or $\begin{cases} \bullet\text{Cl} \\ \bullet\text{H} \end{cases}$	68.5	68.5	?	—
Chloric acid ..	$\begin{cases} \bullet\text{Cl} \\ \bullet\text{Ho} \end{cases}$ or $\begin{cases} \bullet\text{Cl} \\ \text{O} \\ \bullet\text{H} \end{cases}$	84.5	84.5	?	—
Perchloric acid .....	$\begin{cases} \bullet\text{Cl} \\ \text{O} \\ \bullet\text{Ho} \end{cases}$ or $\begin{cases} \bullet\text{Cl} \\ \text{O} \\ \text{O} \\ \bullet\text{H} \end{cases}$	100.5	100.5	?	—

## QUESTIONS AND EXERCISES.

1. Explain the changes which take place when chlorine is passed through a solution of potassic hydrate, 1st, through a dilute solution in the cold; 2nd, through a boiling and concentrated solution.
2. How is bleaching powder manufactured? Express the change by an equation.
3. Give illustrations of the oxidizing action produced by bleaching powder.
4. Under what conditions does calcic chloro-hypochlorite give off oxygen gas?
5. How is "*Eau de Javelle*" prepared, and what are its uses?
6. How are chlorous acid and chlorous anhydride prepared? Describe their properties.
7. Give symbolic and graphic formulæ for sodic hypochlorite, bleaching powder, chlorous anhydride, chloric peroxide, and potassic perchlorate.
8. What changes does potassic chlorate undergo by heat?
9. Describe the method of preparing potassic chlorate on a manufacturing scale.

## CHAPTER XIX.

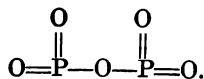
## THE OXIDES OF PHOSPHORUS AND ARSENIC.

PHOSPHORUS, when pure, is a wax-like, faintly yellow, semi-opaque, solid body. It is generally sold in the form of sticks. It melts readily at  $44^{\circ}\text{C.}$ , and becomes then of a yellowish syrupy consistency. It can be distilled, its boiling-point being  $288^{\circ}\text{C.}$  Phosphorus volatilizes, however, far below its boiling-point. Its great inflammability constitutes its most characteristic property. Friction may set it on fire. Dry phosphorus when exposed to the air, combines slowly with oxygen, and its temperature is often raised so considerably by this slow combustion that it melts and inflames spontaneously, especially in warm weather. It has therefore to be preserved in cold water, in which it is quite insoluble.

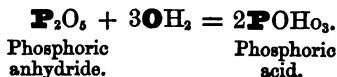
We have already seen (comp. Exp. 23) that phosphoric anhydride results from the combination of phosphorus with oxygen.

**Experiment 147.**—Small quantities of this body may be prepared by burning some phosphorus placed in a little porcelain capsule under a good-sized bell-jar resting on a plate as seen in Fig. 68. The phosphorus should be well dried, and the bell-jar wiped quite dry. A snow-white flaky substance is deposited on the sides of the jar, which may be scraped together with a glass spatula, and kept in a well-stoppered bottle. This white body has a great affinity for water, with which it combines with a hissing noise. On account of its great attraction for water it is often used as a *dehydrating agent*.

Analysis has proved that this white body consists of two atoms of pentad phosphorus, and five atoms of oxygen; hence we write its symbolic formula  $\text{P}_2\text{O}_5$ , and its graphic formula:—



Phosphoric anhydride combines with water to form the hydrated acid, thus:—



There exist three phosphoric hydrates, differing markedly in their properties when in combination with bases.

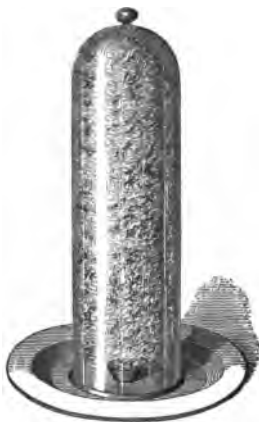
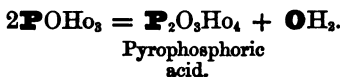
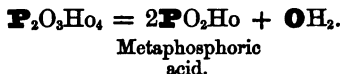


FIG. 68.—COMBUSTION OF PHOSPHORUS.

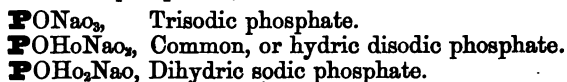
If a solution of phosphoric acid be evaporated in a platinum vessel till it has acquired a syrupy consistency, hard transparent crystals of trihydric acid are obtained. At a higher temperature ( $160^{\circ}$  to  $210^{\circ}$ ) water is given off slowly, and the tetrahydric acid is left, called pyrophosphoric acid (from *πῦρ*, fire), on account of its being produced from the trihydric acid by the application of heat according to the equation:—



At a red heat the pyrophosphoric acid loses a molecule of water, leaving two molecules of the monohydric or metaphosphoric acid, thus:—



The trihydric acid is also called *orthophosphoric acid* (from *ὀρθός*, right), and *common phosphoric acid*, because it occurs in the phosphates most commonly employed in the arts. It contains three atoms of the compound radical hydroxyl, and is capable of forming with the monad radicals potassoxyl or sodoxyl, by the partial or total displacement of the hydroxyl in the acid, three different kinds of salts called orthophosphates, viz.:—



When phosphoric hydrate, or phosphoric acid, is neutralized with sodic hydrate and then evaporated to crystallisation, the second salt is obtained in large transparent, oblique rhombic prisms, which effloresce rapidly in the air. These crystals contain water of crystallisation, and the salt has the composition  $\text{POHoNaO}_2 + 12\text{Aq.}$  (Aq., abbreviation for *aqua*, water, standing for *water of crystallisation*.) A solution of this phosphate gives, with a solution of argentic nitrate, a yellow precipitate of *triargentic phosphate*,—Ago (argenticoxyl) replacing the hydroxyl and sodoxyl, thus:—

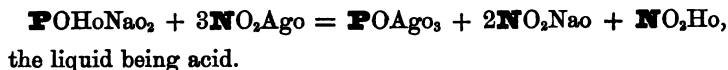


FIG. 69.

**Experiment 148.**—Heat gently a small quantity of the ordinary hydric disodic phosphate in a porcelain dish on a water-bath (Fig. 69). The salt fuses first in its water of crystallisation, then swells up, and gives off puffs of steam, the water escaping from underneath the crust of the solidified salt. Cease heating when no more water escapes, and the liquid salt becomes once more solid. On dissolving a small portion of the white mass in water, and adding a solution of argentic nitrate, the same yellow precipitate will be obtained which the salt gave before being heated. It has not been changed beyond losing its 12 molecules of water of crystallisation. On dissolving in hot water,

and allowing to crystallise, the original rhombic prisms are obtained once more.

Heat some of the dry salt in an iron spoon, or, better, in a platinum vessel, to a strong red heat over a gas flame. Water is again expelled—the water which formed part of the salt, so called water of constitution—and on dissolving a little of the white saline residue in water, and adding a solution of argentic nitrate, a white precipitate is now obtained, and the solution is neutral, an indication that the salt has undergone a change. On dissolving some of the ignited mass in hot water, and setting it aside to crystallise, the solution no longer deposits crystals of the original salt, but of a salt which, on analysis, is found to consist of  $\text{P}_2\text{O}_5\text{Na}_4$  (sodic pyrophosphate).

Its formation is expressed by the equation :—



This salt contains no longer trihydric, but tetrahydric phosphoric acid,  $\text{P}_2\text{O}_5\text{Ho}_4$ , called pyrophosphoric acid.

**Experiment 149.**—We are acquainted with a characteristic salt of ordinary or orthophosphoric acid, called *microcosmic salt*, or hydric ammonic sodic phosphate ( $\text{POHoAmoNa}_3 + 8 \text{Aq}$ ). This salt may be readily prepared by dissolving 6 to 7 parts of the common sodic phosphate of commerce, and 1 part of ammonic chloride in 2 parts of boiling water, and allowing the liquid to crystallise in a cool place. On heating the salt in the same manner as was done in the previous experiment, a clear transparent mass is left, which, if slowly cooled, becomes crystalline; it now deliquesces in air, and dissolves very readily in water. The aqueous solution when almost neutral, gives with argentic nitrate a white precipitate. The supernatant liquid is neutral. Water of crystallisation and ammonia are given off, and the salt,  $\text{PO}_2\text{Na}_3$  (sodic metaphosphate), is left, which contains no longer trihydric, but monohydric phosphoric acid.

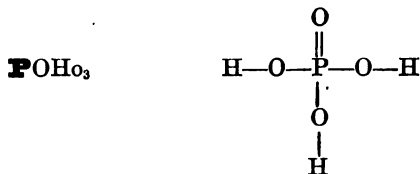
The change may be expressed by the equation :—



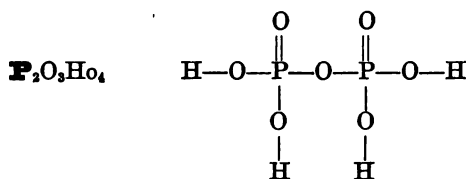
We have thus become acquainted with three modifications of phosphoric acid, not to speak of other forms, viz. :—

1. Common or orthophosphoric acid,  $\text{POHo}_3$  (trihydric or tribasic).
2. Pyrophosphoric acid,  $\text{P}_2\text{O}_5\text{Ho}_4$  (tetrahydric or tetrabasic).
3. Metaphosphoric acid,  $\text{PO}_2\text{Ho}$  (monohydric or monobasic).

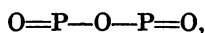
Pentad phosphorus being invariably the grouping element, these acids are written symbolically and graphically, thus :—



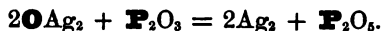




A lower oxide, formed by slow and imperfect oxidation of phosphorus (as when it is exposed to dry air at the ordinary temperature), viz., *phosphorous anhydride*, consisting of two atoms of phosphorus and three atoms of oxygen, is obtained in the form of a white powder possessing the odour of garlic. Its symbolic formula is  $\text{P}'''\text{O}_3$ , its graphic formula:—



the P being in the triad condition, with two bonds left dormant in each atom. Phosphorous anhydride is of interest in so far only as it acts as a powerful reducing agent; i.e., owing to its latent bonds it can deprive other oxides of part of their oxygen. Of the many reactions illustrative of this property, we will only cite the action of  $\text{P}_2\text{O}_3$  on silver oxide, thus:—



Phosphorus is capable of combining also with hydrogen.

**Experiment 150.**—Introduce into a small retort (Fig. 70) some concentrated solution of potassic or sodic hydrate, and a few small pieces of phosphorus. On heating a gaseous body is evolved, which ignites spontaneously as soon as it

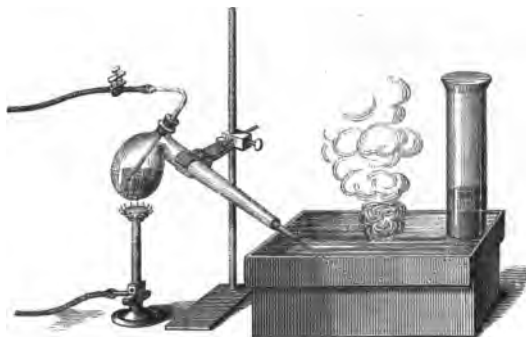
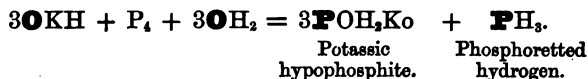


FIG. 70.—PREPARATION OF PHOSPHORETTED HYDROGEN.

issues from the water of the pneumatic trough. Each gas bubble rises through the air with a peculiar circular wreath of white smoke, which enlarges as it ascends in the air. In order to avoid every risk of an explosion, a current of

hydrogen or coal-gas may be passed for some time through the retort previous to applying heat.

Phosphorus alone does not decompose water. It requires the powerful base potassa or soda to induce it to form with the oxygen of the water an oxy-acid, and with the hydrogen an inflammable gas, called *phosphoretted hydrogen*, thus:—



Bodies which appertain to the metals rather than to the non-metals, such as arsenic (As), antimony (Sb), bismuth (Bi), but which form compounds analogous with the compounds of phosphorus, must be briefly glanced at here. These elements are like phosphorus, of a pentad nature. Arsenic, moreover, occurs in nature, closely associated with phosphorus. This close resemblance extends also to the oxides of arsenic and their salts, the *arsenites* and *arsenates*. Two oxides deserve our attention, *arsenious*,  $\text{As}'''\text{O}_3$ , and *arsenic anhydride*,  $\text{As}^v\text{O}_5$ , written graphically:—



In the lower oxide each atom of arsenic has two bonds left unsatisfied; and very interesting reactions, based upon the deoxidation of various higher oxides, by means of arsenious anhydride, result from this property.

Arsenic is sometimes found native, but more frequently in combination with metals, such as iron, nickel, cobalt, etc. When arsenic is combined with metals it forms with them *arsenides*, from which the arsenic can be removed by roasting (in a reverberatory furnace), in the form of a volatile oxide, which is condensed in brick flues, and purified by sublimation.

**Experiment 151.**—Heat a small quantity of some finely powdered arsenide, such as arsenical pyrites, or *mispickel*, in a piece of hard glass tube (combustion-tube), holding the tube in a slightly inclined position, so as to cause a current of air to pass over the ignited powder. The sulphur and arsenic combine with oxygen to form volatile compounds, viz., sulphurous anhydride,  $\text{SO}_2$ , and arsenious anhydride,  $\text{As}_2\text{O}_3$ , leaving the iron as oxide. The  $\text{As}_2\text{O}_3$  condenses in the cold part of the tube, and  $\text{SO}_2$  passes off.

The change takes place according to the equation:—

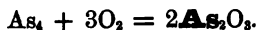
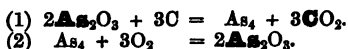


FIG. 71.

**Experiment 152.**—By heating a little of the arsenious anhydride or white arsenic so obtained on charcoal, before the blowpipe (Fig. 71), a strong garlic odour becomes at once perceptible, and white fumes ascend into the air, which are highly poisonous. The experiment should therefore be made with a very small quantity of the substance only, and in a place with a good draught. The charcoal deprives the arsenious anhydride of its oxygen, forming  $\text{CO}_2$  and  $\text{As}$ . The metallic arsenic being readily volatilized, on passing through the outer or oxidizing cone of the blowpipe flame, is partially reconverted into oxide, thus:—



Arsenious differs from phosphorous anhydride by possessing but little affinity for oxygen. It requires, in fact, powerful oxidizing agents, such as nitric acid, to convert it into arsenic acid,  $\text{AsOH}_3$ .

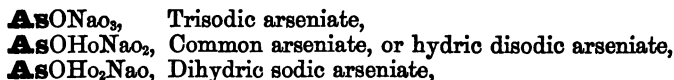
**Experiment 153.**—Dissolve a little powdered white arsenic in a small flask, in hot hydrochloric acid (as it is but slightly soluble in water), and oxidize by means of concentrated nitric acid, as long as ruddy fumes of  $\text{N}_2\text{O}_3$  are evolved. The liquid is then cautiously evaporated to complete dryness, and a little water added to a small portion. The mass dissolves completely, showing a strongly acid reaction to test-paper.

The reaction takes place according to the equation:—

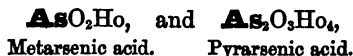


Arsenic anhydride has, like phosphoric anhydride, a great attraction for water. It absorbs moisture from the air, and gradually deliquesces. The solution contains trihydric or tribasic arsenic acid, precisely analogous to orthophosphoric acid, forming salts which are identical in shape (isomorphous) with the corresponding phosphates. A sodic arseniate,  $\text{AsOHoNaO}_2 + 12\text{Aq.}$ , is obtained, when arsenic acid is neutralized with sodic hydrate or sodic carbonate, which cannot be distinguished in appearance from the common sodic phosphate.

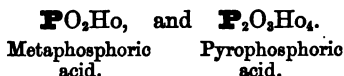
Like phosphoric acid it can form three different kinds of salts, viz.:—



and is capable of retaining one or two parts of unreplaced hydroxyl, or of replacing two parts of hydroxyl by  $\text{Mgo}''$ , or some other oxy-radical of a dyad metal, as in  $\text{AsOAmoMgo}''$ , ammonic magnesic arseniate. Salts are also derived from the acid in which the analogy between arsenic and phosphoric acid is still further borne out. We know salts containing—



Corresponding to—



Arsenious acid forms likewise a definite series of salts, called arsenites, closely analogous to phosphites, of which the alkaline arsenites possess again the greatest interest. The power of forming salts with different bases which this acid possesses is, however, not so well defined as that of arsenic acid.

The compounds which arsenic and antimony are capable of forming with hydrogen, analogous to phosphoretted hydrogen,  $\text{PH}_3$ , viz., arseniethed hydrogen,  $\text{AsH}_3$ , and antimonietted hydrogen,  $\text{SbH}_3$ , will be described in the second Part of this work, under the respective metals.

#### QUESTIONS AND EXERCISES.

1. Describe the most important properties of phosphorus.
  2. How would you prepare small quantities of phosphoric anhydride?
  3. Explain how orthophosphoric, pyrophosphoric, and metaphosphoric acids are obtained. Give equations.
  4. You have given to you a solution of orthophosphoric acid, and a solution of potassic hydrate. State what salts you can form with these materials.
  5. Give symbolic and graphic formulæ for common sodic phosphate, magnesian pyrophosphate, sodic metaphosphate, and phosphorous anhydride.
  6. How would you distinguish between a soluble orthophosphate and pyrophosphate?
  7. Explain the terms, *ortho-* and *pyrophosphoric acid*, *microcosmic salt*, *arsenide*.
  8. Describe the changes which microcosmic salt and the common hydric disodic phosphate undergo, when exposed to a gradually increasing heat. Give equations.
  9. How is phosphorous anhydride prepared, and what is its most characteristic property?
  10. Trace the analogy which exists between phosphorus and arsenic compounds.
  11. What changes do metallic arsenides undergo when heated in a tube of hard glass, open at both ends? Give equations.
  12. How is white arsenic affected when heated on charcoal before the blowpipe flame? Give equations.
  13. In what respect does phosphorous anhydride differ from arsenious anhydride?
  14. What is the action of nitric acid upon arsenious anhydride? Give an equation.
  15. Write out the symbolic formulæ of a few arsenites and arseniates.
  16. How is phosphoretted hydrogen prepared, and what are its most striking properties? Give an equation.
  17. Calculate how much  $\text{NH}_3$  by weight can be obtained upon ignition from 2.350 grms. of  $\text{POAmoMgo}^*$ .
  18. Calculate the percentage composition of microcosmic salt.
-

## CHAPTER XX.

## OXIDE OF BORON.

THE element *boron* occurs in nature always in combination with oxygen, as boric acid, either in the free state or combined with metals. The most important of its salts is *borax*, a compound of the base soda, with boric acid.

**Experiment 154.**—Dissolve a small quantity of powdered borax—the ordinary prismatic crystals of  $\text{B}_2\text{O}_3\text{Na}_2$ —in four times its weight of boiling water, and add to the filtered solution concentrated hydrochloric acid, till litmus-paper is freely reddened. *Orthoboric acid*, or *boric hydrate* separates on cooling in thin translucent pearly plates, which can be obtained in a sufficiently pure state, by pouring off the liquid, washing with a little water, spreading the crystals on filter-paper on a warm tile, and drying at a gentle heat. They are soluble in boiling water, to which they impart only a slight acid taste; and the solution of the acid gives to blue litmus-paper merely a wine-red tint similar to that which carbonic acid produces.

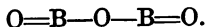
When treated with concentrated hydrochloric acid the sodoxyl radical, it may be assumed, is first acted upon with formation of sodic chloride and  $\text{H}_2\text{O}$ . The five molecules of water (which may be viewed as hydride of hydroxyl,  $\text{HHO}$ ), by attacking five atoms of oxygen, form five molecules of  $\text{H}_2\text{O}$ , and the hydrated acid separates, thus:—



The trihydric or tribasic acid,  $\text{BHO}_3$ , so obtained, is converted into the *metaboric acid*,  $\text{BOHO}$ , by heating up to  $100^\circ \text{C}$ ., thus:—



By exposing the acid to the strongest red heat we obtain *boric anhydride*. This cannot be done without incurring loss from volatilisation. The acid merely fuses and forms, on cooling, a glassy hard ringed mass. The composition of the anhydride is  $\text{B}_2\text{O}_3$ , boron being a triad element. Its graphic formula is written—

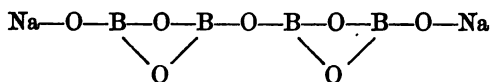


**Experiment 155.**—Dissolve a few crystals of boric acid in a small porcelain dish by means of a little alcohol, and set fire to the spirit. It burns with a green flame, which becomes especially visible on stirring up with a glass rod. A similar green flame is produced if a few crystals of borax are decomposed by the addition of a little sulphuric acid and alcohol, and set fire to as before. This reaction constitutes a characteristic test for boric acid.

Boric acid is principally derived from a mineral called *tincal*, an abnormal sodic borate, having the composition  $\text{B}_2\text{O}_3\text{Na}_2, 10\text{HHO}$ , which may be viewed as a compound of two molecules of sodic metaborate and one molecule of boric anhydride—



Its graphic formula, as expressed by Dr. Frankland, is—



This view is borne out by the facility with which a dilute aqueous solution of borax is decomposed. On adding tincture of litmus to a concentrated borax solution, the liquid acquires a slightly reddish tint, which, on the addition of more water, turns distinctly blue, *i.e.*, on dilution the borax solution acts like a weak solution of a free alkali mixed with boric acid.

Boric acid combines with bases in the state of metallic hydrates, oxides, or carbonates, in many different proportions, both in the wet and dry way. Its salts are called *borates*. At high temperatures it behaves like a strong acid, displacing not only carbonic anhydride, but sulphuric and phosphoric anhydrides, from their salts. In solution, however, boric acid is but a weak acid, although it is capable of combining with free bases, and of decomposing, when in concentrated solutions the metallic carbonates, with evolution of carbonic anhydride, especially on boiling. Its feeble acid character is also manifested in borates containing excess of acid—so-called acid salts—which react strongly alkaline, and in which the feeble acid cannot overcome the alkaline nature of such strong bases as soda or potassa.

**Experiment 156.**—Mix intimately in a mortar some of the boric acid obtained in Exp. 154 with somewhat less than its own weight of sodic chloride, and heat the mixture in a porcelain or platinum crucible over a good gas flame. The mass fuses and a vapour is given off. Remove the lamp for a moment, and hold an inverted bell-jar over the crucible. Strips of blue litmus paper, moistened with water, are made to adhere to the inside of the jar. As soon as the vapour comes in contact with the paper the blue colour changes to red. The vapour consisted of hydrochloric acid. This may be proved by rinsing the jar with a few drops of ammonia, before inverting it over the crucible, when white fumes of ammoniac chloride are formed.

The change takes place according to the equation—



Here, then, is another instance of a curious *reciprocal affinity*. Exp. 154 proved that boric acid is liberated from borax by concentrated hydrochloric acid. The preceding experiment showed that boric acid drives out hydrochloric acid. It is obvious, then, that the affinity of boric acid for soda is greater at a *high* temperature than that of hydrochloric acid; the different action of the two acids is evidently owing to the *fixed* character of the one, and to the *volatile* nature of the other acid—hydrochloric acid being volatile at the ordinary temperature. The tendency in the latter to volatilize at a high heat assisted its escape, whilst the fixedness of the boric acid was actually increased at a melting heat.

Most borates fuse to transparent glasses. Alkaline borates, when fused with metallic oxides, take up and dissolve many of the

latter, forming double borates of the alkali base and the metallic oxide, which are frequently marked by characteristic colours. Hence borax is of great use as a *flux* in metallurgical experiments, or on a small scale, in blowpipe reactions.

#### QUESTIONS AND EXERCISES.

1. What is our chief source of boric acid?
2. How is orthoboric acid obtained from borax? Give an equation.
3. Explain the action of heat upon orthoboric acid.
4. Give symbolic and graphic formulæ for orthoboric and metaboric acid, boric anhydride, borax.
5. What action takes place when orthoboric acid and sodic chloride, or potassic carbonate, are fused together?
6. What is the percentage of boric anhydride in borax?
7. Describe a characteristic test for boric acid.

#### CHAPTER XXI.

#### ON THE BLOWPIPE AND ITS USE.

A useful blowpipe is represented in Fig. 72. It consists of three parts—of a straight tube made of brass or German silver, *a b* (sometimes fitted, for greater convenience, with a horn or ivory mouth-piece); of an air-chamber, *c d*, which arrests any condensed moisture; and of a branch tube, *f g*, which fits into the longer tube, *a b*, at a right angle. The tube, *f g*, is provided with a nozzle, *h*, ending in a platinum jet, which fits somewhat conically over the tube, *f g*, as is shown on a larger scale in Fig. 72, *b*. The most

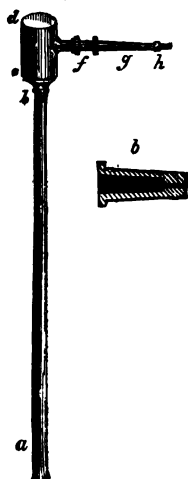


FIG. 72.



FIG. 73.

convenient form of mouth-piece is the trumpet-shaped, whereby blowing is rendered less fatiguing. Other simpler forms of blowpipes have been devised; they require, however, no special description to be readily understood.

The blowpipe is used for conveying a continuous blast of air from the lungs into the flame of a spirit-, gas-, or oil-lamp, or into a candle flame. In any ordinary conical flame we are able to distinguish three different parts, as represented in Fig. 73; 1st, in the middle a dark kernel, *a*; 2nd, a bright cone, *e f g*, surrounding the dark kernel *a*; and 3rd, a feebly luminous outer cone, *b c d*, surrounding the bright cone. The dark part of the flame con-

sists of vapours—principally of compounds of carbon and hydrogen—which burn at the expense of the oxygen of the air. The luminous zone of the candle flame does not get a sufficient supply of oxygen; it is, therefore, the hydrogen which burns chiefly, whilst the hydrocarbon vapour becomes highly heated, and is rendered luminous. In the outer or feebly luminous zone nothing impedes the free access of, and contact with, the atmospheric air; complete combustion takes place; both carbon and hydrogen are converted into their final products of oxidation, into carbonic anhydride and water (steam). This portion of the flame is very hot, the greatest heat being concentrated in the point *c*. If we hold a body, which is capable of taking up oxygen into this outer part of the flame, it becomes rapidly oxidized, since all the conditions are favourable to such a change, viz., a high temperature, and an unlimited supply of air.

The outer zone of the flame forms, therefore, the *oxidizing* flame. If, on the other hand, we introduce a body which is capable of parting with oxygen, into the luminous part of the flame, we should expect to see it become deprived of its oxygen by the hydrocarbon vapours. The body is *deoxygenized* or *reduced* in the luminous zone of the flame; hence this section is called the *reducing* flame.

Now, by introducing a current of air into the interior of a flame, the appearance of the flame changes immediately; it becomes shorter and more pointed in the direction of the current of air. The luminous portion of the flame disappears altogether, and the heat is considerably increased. Two zones of combustion are, in fact, formed, by supplying air to the hydrocarbon vapours; from the inside, as well as from the outside. To produce either an oxidizing or reducing flame, the blast delivered from the blowpipe requires to be properly directed, and must be constant and regular.

While blowing, the trumpet-shaped mouth-piece is pressed *against* the lips, and breathing is effected through the nostrils; the epiglottis is used as a valve. The air must be forced through the blowpipe by the action of the muscles of the cheeks only.

“Beginners, when first practising with the blowpipe, usually commit the fault of not closing the passage between the windpipe and the mouth at the right moment, but of blowing for a longer or shorter period *from the lungs* alone. This mode of blowing, if persevered in, is undoubtedly prejudicial to health; and it is, therefore, advisable that the beginner should practise himself in breathing regularly and audibly through the nose, keeping up a continuous blast by the muscles of the cheeks. This practice should be continued till he is able to do so without any perceptible exertion. In attempting this he will probably not be immediately successful, but a little practice will soon enable him to master this initial difficulty.”—(*Plattner on the Blowpipe*.)

Success in blowpipe operations depends to a great extent upon the lamp we use.

In a laboratory which has a supply of coal-gas, a *Bunsen* burner of the construction shown in Fig. 74 will be found to answer extremely well. The burner rests on a foot of cast-iron, *a b*, into



which a square (or round) block, *c d*, of brass or cast-iron is screwed. This has a cylindrical hole for conveying the air, drawn in through

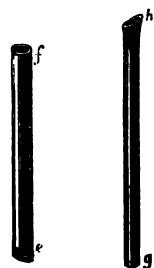


FIG. 74.

four holes into the brass tube, *e f*, which screws either into or over the cylindrical hole. A branch tube, *k*, which can be connected by means of india-rubber tubing with the gas supply, conveys gas to a thin tube with a fine slit, or a couple of fine holes at its upper end, and is screwed into the cylindrical hole. The gas and air mix in the tube, *e f*, and burn at *f* with an almost non-luminous flame. The indraught of cold air keeps the tube cool enough to prevent the flame striking back and burning at the small aperture below.

By introducing, for blowpipe purposes, a narrower tube, *g h*, flattened at the top, into the tube, *e f*, the gas is conveyed from the thin gas delivery-tube below without becoming mixed with air, and burns with its usual luminous flame. On directing a blowpipe jet into the gas flame, the latter is diverted, and we are enabled to produce

either a reducing or an oxidizing flame.

In order to obtain a *reducing flame*, the nozzle (Fig. 75) of the blowpipe is held inclined, almost parallel with the surface of the

flattened top of tube, *g h*, so as just to touch the exterior part of the flame. A more or less yellow flame will be thus produced of the form shown in Fig. 75.

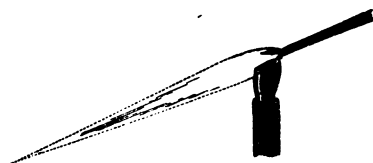


FIG. 75.

ing it somewhat further into the flame (Fig. 76), so as to obtain a clear unbroken jet. A somewhat stronger blast is also sent into the flame, so as to produce a longer and more pointed jet of flame, of a pale blue colour, and almost invisible by daylight. If a *small* fragment of an oxidizable substance be held just *beyond* the point of this flame, it becomes intensely heated, and rapidly absorbs oxygen from the surrounding atmosphere, or,—if the blast from the blowpipe be very strong,—from the air which passed unconsumed through the centre of the flame.

When a substance is submitted to the action of the reducing flame, it should be held so as to be entirely surrounded by the

An *oxidizing flame* is obtained by keeping the nozzle of the blowpipe at the same inclination as before, but introduc-

yellow flame, and protected from the oxidizing action of the atmosphere, but as near as possible to the point of the flame, in order to utilize the greater heat of that part of the jet.

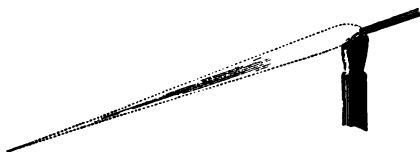


FIG. 76.



FIG. 77.

Far superior to a Bunsen gas-jet is *Herapath's* blowpipe lamp (Fig. 77), constructed on the principle of a Bunsen burner. The gas and air issue from the mouth of the brass jet *well mixed*, and burn, when lighted, with a blue flame. The flame can readily be rendered a reducing one, either by increasing the supply of gas, or by diminishing the blast; or an oxidizing one, by decreasing the gas and increasing the blast of air. By attaching the brass tube by means of flexible india-rubber tubing to a gas supply pipe, and connecting the air-tube with a short piece of tubing ending in an ivory or glass mouth-piece, the lamp becomes a highly serviceable piece of chemical apparatus.

*Supports.*—Charcoal is mostly used as a support in reduction experiments. The best charcoal is that from the wood of the pine, lime, or willow; closely grained, free from knots, and well burnt. The pieces are best cut by a small-toothed saw into regular prisms of about six inches in length, and from one to two inches in breadth, having a flat smooth surface at right angles to the lines of growth, because the fluxes spread out on the charcoal on the other surfaces (*Berzelius*). A good piece of charcoal may be made to serve for many experiments, by simply filing off the used surface and exposing a new one after each operation.

What renders charcoal so valuable as a support in blowpipe experiments is, 1st, its infusibility; 2nd, its weak power for conducting heat; 3rd, its porosity, which enables it to absorb within its pores readily fusible fluxes, such as borax, microcosmic salt, sodic carbonate, potassic cyanide, leaving the infusible substance under examination behind; and, lastly, its power of assisting in the reduction of oxidized substances in the inner blowpipe flame, on account of the carbonic oxide atmosphere which the charcoal furnishes by the partial combustion of its carbon.

The substance to be subjected to the blowpipe flame (which if a powder should be previously moistened with a little water to

make it cohere) is placed in a shallow cavity, scraped out near the end of the charcoal, and the latter is so held that the flame impinges upon the substance at a slight angle, as seen in Fig. 71.

*Platinum wire*, frequently also *platinum foil*, or a small platinum spoon, is employed for oxidation experiments, or for the diffusion of insoluble bodies in fluxes, in order to observe the coloured glasses which they produce.

Thin platinum wire is chosen, which may be used in the form of a coil, with the ends unrolled, or in pieces about half a foot in length (Fig. 78). These are fused for convenience, sake into a piece of glass tubing drawn out to a point, with the end turned into a hook or loop, to hold the borax or microcosmic salt which is to be fused into a bead. (Care must be taken that no substance, such as sulphur, lead, etc., which acts upon platinum, be fused upon the wire.)

*Platinum foil* is employed as a support for substances which are not to be exposed to the reducing action of charcoal. The foil may be placed on a piece of charcoal, or held in the flame by a pair of forceps.

*Platinum Spoon*.—This should be of the size and form shown in Fig. 79. It may either be fixed into a wooden handle or into a cork. (The lid of a small platinum crucible, supported on a platinum triangle (Fig. 80), answers equally well.) It is used for fusing certain substances with alkaline carbonates, hydric potassic sulphate ( $\text{SO}_2\text{HoKo}$ ), or nitre ( $\text{NO}_2\text{Ko}$ ).



FIG. 78.



FIG. 79.

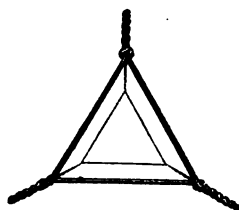


FIG. 80.

*A pair of Brass Forceps with Platinum Tips*.—These are constructed as shown in Fig. 81. A fragment of the mineral or other substance is held between



FIG. 81.

the platinum points, *a*, which are opened by pressing on the knobs, *b b*, and close again by their own elasticity.

These forceps are used for holding splinters of minerals, etc., which are to be heated in the outer or hottest part of the blowpipe flame, to ascertain their fusibility and the colour they impart to the blowpipe flame.

**Experiment 157.**—Heat on a charcoal support a little litharge (plumbic oxide,  $PbO$ ) in the reducing flame of the blowpipe. Globules of metallic lead are left, and a yellow *incrustation* forms on that part of the charcoal over which the flame passes.

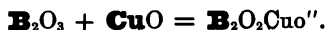
This arises from the deposition of yellow plumbic oxide on the cooler parts of the charcoal. Some of the metal is, in fact, volatilized, and on passing through the outer flame of the blowpipe is oxidized. The same occurs in the case of other metals; hence the different and often characteristic incrustations, observed when metallic oxides are heated on charcoal in the reducing flame, frequently help to distinguish such metallic bodies in a very ready manner.

**Experiment 158.**—Heat a small piece of metallic antimony in the cavity of the charcoal in the oxidizing flame of the blowpipe. The metal melts readily, and gives off white fumes, and a white deposit of antimonious oxide,  $Sb_2O_3$ , covers the charcoal all round the metallic antimony, which by continued heat may be entirely volatilized.

Most metals (with the exception of gold and platinum) are capable of being converted into oxides, when heated in the outer flame of the blowpipe.

**Experiment 159.**—Melt some borax on the loop of the platinum wire to a clear pearl of borax glass. The bead should be perfectly colourless, both in the hot and cold state. While the glass is still hot and fluid, it is brought in contact with a small quantity of black cupric oxide, and the outer flame of the blowpipe applied a second time. The black oxide dissolves in the liquid glass, and produces a deep dark colour. If introduced in small quantities the glass is *green* whilst hot, and *blue* on cooling; if in large quantities the green colour is so intense as to appear black; when cool this becomes paler, and changes to a greenish-blue. When heated in the reducing flame the copper glass becomes nearly colourless, but immediately on solidifying assumes a red colour, and becomes opaque from the separation of metallic copper. By long continued blowing on charcoal the oxide is reduced, and the metal separates in the form of a small metallic bead, leaving the glass colourless.

The change which takes place will be readily understood after what has been stated in Chapter XX with regard to the action of borax at high temperatures. The molecule  $B_2O_3$  forms with the  $CuO$  a cupric metaborate, thus—



In performing this experiment, and experiments of a similar nature, care must be taken not to dissolve, in the first instance, too large an amount of the oxide, or other substance under examination. If a small quantity affords no distinct reaction, more may be easily added. If, however, the colour of the bead be too intense to be clearly distinguishable, the bead may be jerked off from the wire, and the portion which still adheres fused up with a fresh quantity of borax, in which manner a more dilute bead will be obtained.

We possess in microcosmic salt another most valuable flux, as it leaves, on ignition, sodic metaphosphate, a readily fusible salt. The action of this salt is analogous to that of borax; but as experience has proved that the beads which it forms with many

substances are more characteristic, and the colours better defined than those produced by borax glass, it is frequently preferred to the latter as a flux.

Microcosmic salt, when fusing at first in its eight molecules of water of crystallisation, is so fluid that it readily drops from the platinum loop. It is, therefore, advisable to fuse it on charcoal or platinum foil, when the water and ammonia are driven off, and a viscid residue is left. Some of the glass thus formed can readily be taken up on the platinum wire (the loop may be made somewhat smaller), and the powdered mineral or oxide fused with it in the same way as with borax.

**Experiment 160.**—Dissolve a little uranic oxide,  $\text{U}_2\text{O}_5$ , in a bead of microcosmic salt. It dissolves to a clear yellow glass in the outer flame, and becomes yellowish-green on cooling. Heated in the reducing flame the glass assumes a beautiful green colour, which becomes more brilliant as the bead cools.

The action of the sodic metaphosphate consists in taking up metallic oxides, and forming with them tribasic phosphates, containing more than one base.

The blowpipe is of great assistance in chemical analysis, because it individualizes the body under examination, by producing distinctive changes, which are peculiar for the most part to each of the metals. Although the presence of other bodies may interfere to some extent with the special reactions of the body for which we search, and thus render the search doubtful or in some cases nugatory, it cannot be too strongly impressed upon the chemical student to gain a complete mastery over the blowpipe reactions, as being by far the most easy and readily available means of qualitative analysis.

#### QUESTIONS AND EXERCISES.

1. Describe the construction of the mouth blowpipe.
2. Describe the nature of a candle flame.
3. Describe the construction of a *Bunsen* gas-burner.
4. Explain the oxidizing and reducing action of the blowpipe flame. Give examples.
5. Explain the use of borax and microcosmic salt in blowpipe reactions.

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### CHAPTER XXII.

#### ON SILICA AND SILICATES.

*Silica* is one of the most widely diffused substances in nature, and constitutes, together with the compounds which it forms with metallic bases, viz., the *silicates*, the greater part of the solid crust of our earth.

It is found either in the *free* or *combined* state. White and yellow sand, quartz, agate, flint, rock-crystal, opal, chalcedony, are more or less pure silica.

**Experiment 161.**—Add dilute hydrochloric, nitric, or sulphuric acid to a solution of so-called *water glass* (sodic silicate). Gelatinous silicic hydrate separates, which may be thrown on a filter and washed with water, in which medium it is but slightly soluble. Dry the precipitate by placing the funnel on a hot sand-bath over a filter drier (Fig. 82). The gelatinous mass shrinks together considerably. It loses its water and becomes anhydrous, even at the temperature of boiling water. Remove the precipitate, when dry, from the filter, and heat it strongly in a porcelain or platinum crucible. A fine white amorphous powder is left, perfectly insoluble in water.



FIG. 82.

Analysis has proved that this white powder consists of one atom of the element silicon and two atoms of oxygen; it is called silica, or *silicic anhydride*,  $\text{SiO}_2$ . Silicon being combined with two atoms of oxygen must be a tetrad element, and silica is written graphically—

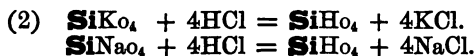


**Experiment 162.**—Mix some *finely powdered*\* quartz intimately with about four times its weight of *fusion mixture* ( $\text{CONa}_2$  and  $\text{COKo}_2$ , mixed in molecular quantities) and heat in a covered platinum crucible over the flame of a Bunsen lamp. The mixture fuses, if sufficient heat be applied, and gives off bubbles of carbonic anhydride. Heat as long as any gas comes off, and keep the contents of the platinum crucible from ten minutes to a quarter of an hour in a state of quiet fusion; allow to cool, and remove the solidified mass from the crucible by digesting for some time with hot water in a porcelain dish. The whole of it dissolves. This proves that the quartz was completely fused. (A successful fusion can only be effected by powdering the quartz in the first instance very finely.) Acidulate the solution now with dilute hydrochloric acid; carbonic anhydride is evolved, owing to the decomposition of the excess of the alkaline carbonates, and gelatinous silica separates. Evaporate to complete dryness on a water-bath. Stir the gelatinous mass which is left with a stout glass rod, and break up the lumps. Transfer the dish for a short time to a hot sand-bath, and apply a somewhat stronger heat. Set it aside to cool, and treat with a few drops of concentrated hydrochloric acid. Allow the acid to soak for some time, and then add hot water. Filter the insoluble residue, wash well, dry, and ignite gently in a porcelain or platinum crucible. A dazzling white powder of *silicic anhydride* will be left.

The changes may be expressed symbolically by the following equations:—



Fusion mixture.



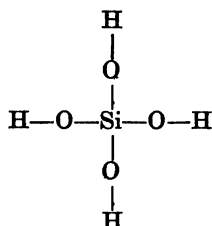
Silicic hydrate.



Silicic anhydride.

Silicic acid (also called orthosilicic acid) is a *tetrabasic* acid, being combined with four atoms of Ho. It is written graphically—

\* Hard substances, such as quartz, should be powdered in an agate mortar.



A *dibasic* acid is said to be produced by the evaporation *in vacuo* at 16° C., of a solution of the tetrabasic acid in water—



This acid is of little interest.

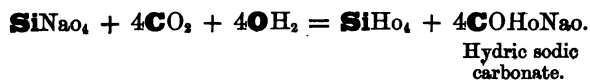
Silicic acid is an extremely indifferent body; it is inodorous and tasteless, and has scarcely any action upon vegetable colours (litmus). It combines with bases in the wet way with great difficulty, and forms amorphous salts. Like boric acid it is affected quite differently at a high temperature.

**Experiment 163.**—Heat a mixture of powdered nitre ( $\text{NO}_3\text{Ko}$ ) with finely powdered quartz in a platinum crucible over a good gas flame; ruddy fumes are seen to escape. The nitric anhydride is displaced by the silicic anhydride, and breaks up as soon as it is liberated from the nitre into  $\text{N}_2\text{O}_4$  and O.

Silicic anhydride, therefore, liberates nitric anhydride from its salts. A similar action takes place when sodic chloride is employed instead of nitre.  $\text{SiO}_2$  can even drive out  $\text{SO}_3$  (e.g., from  $\text{SO}_3\text{Na}_2$ ), especially when heated with it in the presence of charcoal; and yet in Exp. 161 it has been shown that silicic hydrate can be separated from sodic silicate by dilute hydrochloric acid.

Silica in this respect resembles boric acid. It exhibits at different temperatures the same curious *reciprocal affinity*, for it can be displaced from its saline combinations by hydrochloric acid, etc., or may itself displace at a high temperature,—owing to its fixed character,—volatile acids, such as carbonic, nitric, hydrochloric,\* sulphuric acid. On passing carbonic anhydride through a solution of sodic silicate, gelatinous silicic acid separates in flakes.

The reaction takes place according to the equation—



It is, no doubt, owing to this action of carbonic anhydride upon silicates, that many spring waters contain small quantities of silicic acid in solution.

Different kinds of glass, colourless or coloured, may be made on a small scale by fusing before the blowpipe flame a *small* quantity

\* By heating the mixture of  $\text{SiO}_2$  and  $\text{NaCl}$  in a current of steam.

of sodic carbonate, together with some white sand, and by dipping the clear bead into various metallic oxides, and heating once more.

Porcelain fire-clay, bricks, tiles, stone-ware, pottery, etc., consist mainly of aluminic silicate.

A great many minerals consist of silica and earthy and metallic bases in varying proportions.

#### QUESTIONS AND EXERCISES.

1. How does silica occur in nature?
2. How can silicic anhydride be prepared from a solution of water-glass?
3. How is white sand converted into potassic silicate?
4. Give symbolic and graphic formulæ for silicic anhydride and silicic acid.
5. How would you show experimentally that silica can displace  $\text{N}_2\text{O}_5$  or  $\text{SO}_3$  from their respective sodic salts?
6. Explain the action of  $\text{CO}_2$  upon a weak solution of sodic silicate.
7. What substances enter chiefly into the composition of porcelain, fire-clay, stone-ware?
8. How much  $\text{SiO}_2$ , and how much  $\text{CONaO}_2$  are required to manufacture 100lb. of water-glass?
9. 1.235 grm. of fire-clay yielded .793 grm. of  $\text{SiO}_2$ ; what is the percentage of silica in the clay?

### CHAPTER XXIII.

#### GENERAL PROPERTIES OF SALTS.

THE *solubility* of different salts in water varies very much. Some salts, such as calcic chloride,  $\text{CaCl}_2$ , magnesian chloride,  $\text{MgCl}_2$ , cannot be left exposed to the air even, without attracting moisture very rapidly; they are deliquescent. Others, such as calcic carbonate,  $\text{CaCO}_3$ , have no attraction for water. Certain salts dissolve in water, others are insoluble. Almost all salts which are soluble in water dissolve more freely and more extensively in boiling than in cold water. A solution is said to be *saturated in the cold*, when no more of the salt dissolves in it; a *hot saturated* solution, when boiling water has dissolved as much of a salt as will dissolve.

**Experiment 164.**—Dissolve some common salt in hot water in a porcelain dish, and raise the temperature at last to boiling. Plunge a thermometer into the liquid. The mercury rises rapidly above  $100^\circ\text{C}$ .—the temperature of boiling water. A *saturated* boiling solution of sodic chloride indicates in fact a temperature of  $108^\circ$ — $109^\circ\text{C}$ .

The boiling-point of saturated solutions, and the percentage of solubility of a few well known salts, are here annexed—



Name of salt.	Parts by weight of salt dissolved in 100 parts of water.	Boiling point of saturated solution.
Potassic chlorate .....	61.5	104.2° C.
Baric chloride .....	60.1	104.4° "
Sodic carbonate.....	48.5	104.6° "
Potassic chloride .....	59.4	108.3° "
Sodic chloride .....	41.2	108.4° "
Ammonic chloride.....	88.9	114.2° "
Potassic nitrate.....	335.1	115.9° "
Strontic chloride .....	117.5	117.8° "
Sodic nitrate .....	224.8	121.0° "
Potassic carbonate.....	205.0	135.0° "
Calcic nitrate .....	362.0	151.0° "
Calcic chloride .....	325.0	179.5° "

It appears that in most instances the boiling-point is directly proportionate to the solubility of a salt.

On allowing a saturated boiling solution to cool, some of the salt *crystallises* out, and the crystals will be all the more perfect the slower the solution cools. In order to get good crystals, saline solutions are set aside for spontaneous evaporation. The solution should, of course, be well protected from dust, by being kept carefully covered with filter-paper. In consequence of the constantly increasing concentration of the saline solution by slow evaporation in the air, the crystals have plenty of time to form regularly, and to grow slowly, till at last nearly the whole of the salt has been withdrawn from the solution. The remaining liquid may then be poured off from the crystals; it is called the *mother-liquor*. Growing crystals may actually be fed with a fresh portion of the saline solution, till they have acquired a considerable size.

**Experiment 165.**—Make a hot saturated solution of the well known salt *alum*. Allow it to cool. Then pour off from the crystals the still warm mother-liquor into a previously warmed porcelain dish, and set aside for crystallisation. When cold, pour off the mother-liquor, and pick out a few of the best crystals. They are *octahedral* in shape. One or more of these octahedra are then put into the cold saturated mother-liquor, and the crystal turned over on a fresh side every day, till after eight days it has rested on every one of the eight sides. It grows during this time, and attains considerable size, whilst the form of crystallisation remains the same.

If the crystal were not turned, it would likewise grow, but not regularly; for no deposit of saline matter can take place on the side on which it lies, nor on the side diametrically opposite to it. It would acquire what is called the *truncated octahedral* form. Instead of turning the crystals over, day after day, they may be allowed to form on a piece of fine string, from which they are conveniently suspended in the mother liquor, and left to grow slowly.

*Crystallisation* furnishes us with the means of *purifying soluble salts* from foreign substances. It is easy to purify salts soluble with difficulty from salts which dissolve freely in water, such as potassic carbonate, calcic chloride. Smaller crystals, as a rule, are purer than large crystals, because some of the mother-liquor is apt to be locked up within the interstices of the latter. Thus com-

mercial nitre or saltpetre contains small quantities of potassic chloride and sulphate, which can only with difficulty be removed by repeated recrystallisation: but they are readily eliminated by constantly stirring a hot solution of the impure salt whilst it cools, as long as a fine powder (called *saltpetre flour*) of potassic nitrate falls out. The impurities are left in the mother-liquor.

Many salts combine chemically, the moment they crystallise, with a certain quantity of water, called *water of crystallisation*. This appears to be essential to their existence in a crystalline condition, and materially influences their structure; for on expelling the water by heat, the crystals crumble down to a powder. The anhydrous powder attracts water again very eagerly, and such dehydrated salts are frequently employed to deprive certain liquids, such as spirits of wine, etc., of water.

A great number of salts unite with the same amount of water of crystallisation under identical conditions of temperature and saturation: and the molecular units of water of crystallisation are reducible to simple constant proportions, and follow the law of constant chemical combining proportions, as much as compounds of two or more elements.

**Experiment 166.**—Heat a few grammes of *blue vitriol*, or cupric sulphate ( $\text{SOH}_2\text{CuO}''$ , 4 aq.) cautiously in a porcelain dish. The salt fuses in its water of crystallisation, or it undergoes what is called the *aqueous fusion*. It is dihydric at about  $100^\circ\text{C}$ . Keep stirring with a glass rod, till the water of crystallisation has been driven off, and till the blue salt has nearly turned white. On adding a little water to a portion of the powder, and stirring, it acquires its blue colour again. Much heat is given off at the same time.

**Experiment 167.**—To another portion of the white powder add a little alcohol (methylated spirit). The blue colour is likewise restored. The alcohol must have become deprived of its water. In this manner weak alcohol may be rendered almost *absolute*, i.e., free from water.

The *evolution of heat* which accompanied the combination of the white powder with water, points to an actual *chemical* combination between the water of crystallisation and the salt.

On exposing the white powder to a stronger heat (about  $200^\circ\text{C}$ .), another molecule of water is given off, which is evidently combined differently from the four molecules of water of crystallisation. It is termed *water of constitution*.

The water of crystallisation of a salt, obtained from one and the same saturated solution, frequently varies with the temperature, e.g., sodic sulphate ( $\text{SO}_2\text{NaO}_2$ ) when allowed to crystallise from its solution at a temperature of  $33^\circ\text{C}$ ., retains ten molecules of water, and yields anhydrous crystals above that temperature.

Manganous sulphate ( $\text{SO}_2\text{MnO}''$ ) crystallises from its aqueous solution with six molecules of water of crystallisation at  $15^\circ\text{C}$ . It has the composition  $\text{SOH}_2\text{MnO}'' + 6\text{aq}$ . Between  $15^\circ\text{C}$ . and  $30^\circ\text{C}$ . it crystallises with five, and between  $30^\circ\text{C}$ . and  $40^\circ\text{C}$ . with four molecules of water of crystallisation. The crystals belong respectively to the rhombic, triclinohedric, and monoclinohedric systems. It follows that the molecules of water of crystallisation are capable of modifying the character of salts as much as their other constituent

elements. The last molecule of water—the water of constitution—is only driven off at  $200^{\circ}\text{C}$ .

**Experiment 168.**—Expose a few crystals of *washing-soda* ( $\text{CONa}_2 + 10\text{ aq.}$ ), for some time to the air. They become opaque, and crumble at last to pieces. The salt loses its water of crystallisation, even at the common temperature, but more rapidly when gently heated.

The same is observed when *green vitriol* ( $\text{SOHo,Feo}'' + 6\text{ aq.}$ ), hydric disodic phosphate ( $\text{POHoNa}_2 + 12\text{ aq.}$ ), sodic sulphate ( $\text{SO}_2\text{Na}_2 + 10\text{ aq.}$ ), and other similarly constituted salts are exposed to the air. These salts are said to be *efflorescent*.

Salts which have been allowed to crystallise from water at the ordinary temperature, and have consequently taken up as much water of crystallisation as they possibly can,—produce *cold*, when their crystals are redissolved, either at the same or at a higher temperature; because they absorb heat from the water on passing from the solid to the liquid state. Heat must, therefore, have become transferred, in the one instance, from the dehydrated salt to the water (which has already as much heat as it can bind), and heat is therefore given off: in the other instance from the water to the crystalline salt, the latter depriving the water of heat. On mixing some salts or a mixture of certain salts in definite proportions with water, a considerable degree of *cold* may be produced. Mixtures of this kind are called *freezing mixtures*.

**Experiment 169.**—Mix one part by weight of crystallised sodic carbonate with one part by weight of water at  $10^{\circ}\text{C}$ ., and ascertain by the aid of a thermometer that the temperature of the water is lowered from  $10^{\circ}\text{C}$ . to  $-14^{\circ}\text{C}$ .

Numerous other salts may be employed with like effect.

**Colour of Salts.**—Most salts are *solid* bodies at an ordinary temperature. Salts obtained by the action of a colourless acid upon a colourless base are likewise *colourless*. Coloured bases produce for the most part coloured salts on combining with colourless acids; and the crystalline salts mostly resemble the original base in colour. Salts formed by the combination of a colourless base with a coloured acid generally exhibit the colour of the acid from which they are derived.

**Taste of Soluble Salts.**—The taste which various salts exhibit is for the most part dependent upon the constituent base. Thus, sodic salts possess a purely saline taste, not unlike that of common salt; potassic salts possess a saline, and somewhat bitter taste. Magnesian salts have a nauseous bitterness; aluminic salts an astringent sweet taste, etc. The taste is also influenced by the acid which the salts contain, as in sulphites and salts of metallic acids.

#### QUESTIONS AND EXERCISES.

1. Give instances of deliquescent salts.
2. How would you prepare a saturated solution of a salt?
3. What general relation is there traceable between the solubility of salts and the boiling points of their saturated solutions? Give instances.
4. How are salts soluble in water purified?

5. Explain the terms *mother-liquor*, *aqueous fusion*, *water of constitution*, *efflorescent*, *freezing mixture*.
6. How would you prepare octohedral crystals of alum?
7. How is saltpetre freed from potassic chloride and sulphate?
8. Give the symbolic formulæ of blue vitriol, green vitriol, crystallised manganous sulphate.
9. Explain what takes place when blue vitriol is heated—1st, to 100° C.; 2nd, to 200° C.
10. What is the action of dehydrated cupric sulphate upon ordinary proof spirits (containing 50 per cent. of alcohol)?
11. On what considerations would you select the materials for making a freezing mixture?
12. Explain the cause of the colour which various salts exhibit.
13. What influences the taste of salts?
14. How would you determine experimentally the percentage of water of crystallisation in a salt?
15. Three grms. of washing-soda lost 1.888 grm. of water on drying and ignition: what is the percentage of water of crystallisation, and how would you calculate the formula of the crystalline salt from these numbers?

## CHAPTER XXIV.

## REACTION OF SALTS.—NORMAL, ACID and BASIC SALTS.—DOUBLE SALTS.

ON adding a solution of potassic hydrate to sulphuric acid (comp. Exp. 44), we obtained a *salt* which was *neutral* to litmus paper,\* *i.e.*, it did not turn blue litmus red nor red litmus blue. Now, potassic hydrate has a strongly alkaline, and sulphuric acid a strongly acid reaction: and it would, therefore, appear as if one of the most characteristic signs of the *saline* nature of a body consisted in its neutral reaction. This applies, however, only to a very limited number of salts, such as potassic nitrate ( $\text{NO}_3\text{Ko}$ ), sodic nitrate ( $\text{NO}_3\text{Na}$ ), sodic sulphate ( $\text{SO}_4\text{Na}$ ), magnesian sulphate ( $\text{SO}_4\text{Mg}$ ), calcic sulphate ( $\text{SO}_4\text{Ca}$ ), baric nitrate ( $(\text{NO}_3)_2\text{Ba}$ ). By far the greater number of salts, in fact most soluble sulphates and nitrates, have the power of reddening blue litmus, *e.g.*, ferrous sulphate ( $\text{SO}_4\text{Fe}$ ), zincic sulphate ( $\text{SO}_4\text{Zn}$ ), manganous sulphate

\* Litmus is a vegetable colouring matter consisting of a true salt of a mineral base and a vegetable acid. On adding to a solution of litmus in water a mineral acid, the organic salt is decomposed, and the organic acid liberated. This acid possesses great tinctorial power, and is of a light red colour. A weak acid deprives the blue salt only of one-half of its base; leaving a salt, containing excess of the organic acid, and imparting to the solution a peculiar wine-coloured tint. On the addition of a soluble base, the red solution turns blue again, because the base combines with the acid to form a blue salt.

A sensitive litmus solution should not, therefore, contain any free base, because acids would first neutralize this latter before they could liberate the acid contained in litmus. A solution of red litmus is obtained by adding very dilute sulphuric acid, by means of a glass rod, till the blue of the litmus is changed to a distinct red. Such a solution is turned blue on coming in contact with the least trace of a soluble base.

( $\text{SO}_2\text{Mno}''$ ), cupric sulphate ( $\text{SO}_2\text{Cuo}''$ ). Others, again, turn red litmus-paper blue; e.g., sodic and potassic carbonates, borax, etc. Hence there are salts which react *neutral*; others which react *acid* or *alkaline*, and in which the acid reaction does not arise from any *free* or *uncombined acid* in the salt, nor the alkaline reaction from any *free alkali*, but in which the reaction is due rather to the relative *strength* of the acid and basic constituents which enter into the saline body.

The powerful sulphuric acid, for instance, can only just neutralize the strong alkali, potassa; and when in combination with weaker bases, such as the oxides of the metals proper (which, as we have seen repeatedly are without reaction on litmus-paper), it impresses its acid character upon the salts. The same applies to the salts which nitric and other mineral acids form.

Weak acids, such as carbonic, boric, and silicic acid, on the other hand, are not capable of entirely neutralizing strong alkaline bases, such as potassa and soda: their saline compounds react alkaline. It is impossible, therefore, to infer the preponderance of acid or base in a salt from the reaction, if any, which it possesses; for in solutions of salts, such as—

$\text{SO}_2\text{Nao}_3$ , and $\text{SO}_2\text{Cuo}''$ ,
Sodic sulphate      Cupric sulphate
(neutral).              (acid).

—salts which exhibit neutral and acid reactions, and which are formed by the displacement of the hydrogen of the sulphuric acid by atomic amounts of the metals sodium and copper,—the same amount of acid causes the one salt to become neutral, the other acid.

If we take a *salt\** to be the product of the mutual action of an acid and a metal or base upon each other, *normal salts* are obtained by exchanging the whole of the replaceable hydrogen of the acid for an equivalent amount of a metal, or of a positive compound radical, such as ammonium,  $\text{NH}_4$ .

Instances of normal salts :—

Salts.	Acid from which the salt is derived.
$\text{NO}_2\text{Ko}$ , neutral reaction. ....	$\text{NO}_2\text{Ho}$ .
$\text{SO}_2\text{Nao}_3$ , " " .....	$\text{SO}_2\text{Ho}_2$ .
$\text{SO}_2\text{Cao}''$ , " " .....	$\text{SO}_2\text{Ho}_2$ .
$(\text{NO}_2)_2\text{Coo}''$ , acid reaction .....	$\text{NO}_2\text{Ho}$ .
$\text{NOKo}$ , alkaline reaction .....	$\text{NOHo}$ .
$\text{SO}_2\text{Zno}''$ , acid reaction .....	$\text{SO}_2\text{Ho}_2$ .
$\text{PONao}_3$ , alkaline reaction .....	$\text{POHo}_3$ .
$(\text{PO})_2\text{Cao}''_3$ (insol. in water) .....	$\text{POHo}_3$ .
$\text{BNao}_3$ , alkaline reaction .....	$\text{BHo}_3$ .
$\text{SiNao}_4$ , " " .....	$\text{SiHo}_4$ .

\* Frankland : Lecture Notes, page 12.

An **acid salt** is obtained when two or more atoms of replaceable hydrogen are only partially exchanged for the metal or positive compound radical.

The following are illustrations of acid salts—

Salt.	Acid.
<b>SO<sub>2</sub>HoKo</b> , acid reaction.....	<b>SO<sub>2</sub>Ho<sub>3</sub></b> .
<b>COHoKo</b> , alkaline reaction .....	( <b>COHo<sub>3</sub></b> ) ?
<b>POHoNaO<sub>3</sub></b> , alkaline reaction.....	<b>POHo<sub>3</sub></b> .
<b>AsOHoKo<sub>2</sub></b> , alkaline reaction .....	<b>AsOHo<sub>3</sub></b> .
<b>SOHoNaO</b> , acid reaction.....	<b>SOHo<sub>3</sub></b> .

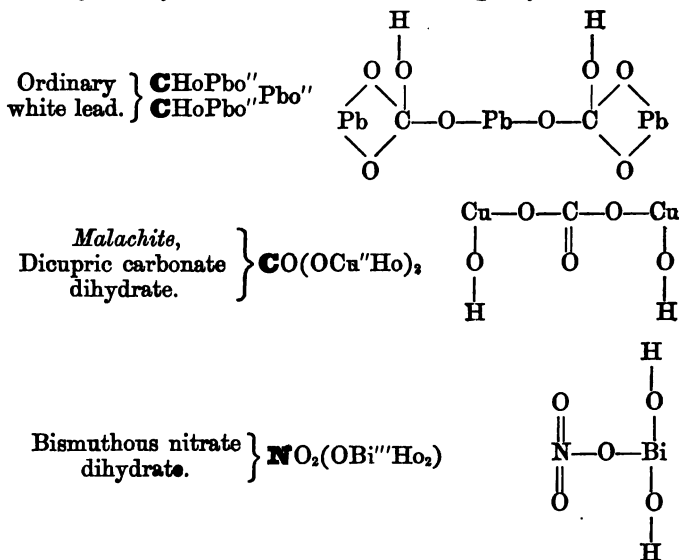
Monobasic acids form normal salts. Di-, tri-, and tetra-basic acids only can form acid salts. Dyad elements replacing H<sub>2</sub> in dibasic acids exclude the possibility of acid salts, unless two molecules of acid enter into the reaction.

The reaction with litmus is obviously no criterion of the normal or acid constitution of a salt.

"When the number of bonds of the metal or compound positive radical in a salt exceeds the number of atoms of displaceable hydrogen in the acid, the compound is usually termed a **basic salt**," ex. gr.

*Symbolic formulæ.*

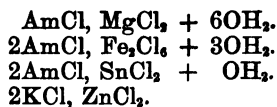
*Graphic formulæ.*



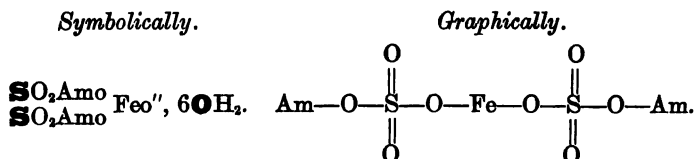
**Double Salts.**—There exists a class of salts called double salts, containing *one* acid only, but *two different* bases, and quite distinct from the acid salts just explained. The base ammonia is especially remarkable for its tendency to form double salts.

Chemists are compelled to admit in these double salts, and in salts containing water of crystallisation, a mere *molecular union* or *molecular combination*. This, in chemical notation, is distinguished from atomic combinations by the use of the comma. In all cases molecular combination seems to be of a much more feeble character than atomic union.

The following are instances of double salts, in which a mere molecular combination is traceable:—

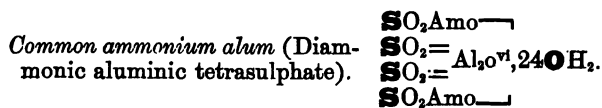


Other double salts are formulated atomically, thus—

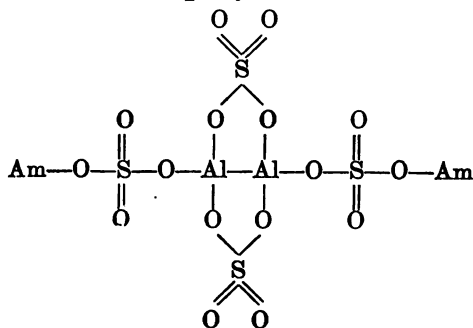


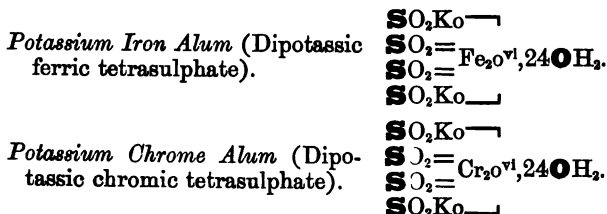
In like manner an important group of double salts is formed by the combination of the sulphates of the metals aluminium, chromium, iron, manganese, with the alkaline sulphates. They have received the name of *alums* from the resemblance which they have to common alum, a salt known long before the others were prepared.

Examples of alums we have in—



*Graphic formula.*





These double salts are remarkable for the facility with which they crystallise and for the size and beauty of their crystals.

#### QUESTIONS AND EXERCISES.

1. Give instances of salts which react neutral, acid, or alkaline with litmus-paper; and assign reasons for the reaction which different salts give.
2. Define normal, acid, and basic salts; give instances of each class of salts.
3. Why can litmus not be employed in order to ascertain whether a salt is a normal or acid salt?
4. What is a double salt?
5. Give instances of double salts in which only a molecular combination can be traced.
6. Enumerate some double salts in which an atomic union is apparent.
7. What is an alum? Give names, as well as symbolic and graphic formulæ of different alums.
8. Write out the symbolic and graphic formulæ for hydric sodic sulphite, white lead, and *malachite*.
9. Explain in what combination water of crystallisation is considered to exist in salts.
10. You have given to you hydric potassic sulphate and saltpetre. Explain how you would demonstrate experimentally that one of these salts is an acid salt.

#### CHAPTER XXV.

#### DEFINITION OF CHEMISTRY.—MODES OF CHEMICAL ACTION.

CHEMISTRY has been defined "as the science which treats of the composition of all kinds of matter, and of those changes in composition which result from the action either of different kinds of matter upon each other, or of external forces upon one and the same kind of matter."\*

Chemical changes depend upon the affinities with which every kind of matter has been endowed by nature: they are modified more or less by the temperature, and by the state of aggregation—solid, liquid, or gaseous—of the simple or compound bodies.

\* Frankland: Lecture Notes, page 1.



*Matter undergoes a chemical change\*—*

**I. When an element combines with another element in simple or multiple proportions to form a compound body: e.g.,**



Numerous other oxides are formed in like manner, as illustrated by experiments:—6 (28, 37, 39, and 40), 10 (and 41), 11 (19 and 42), 12 (and 20), 13 (and 21), 14, 15, 22 (and 48), 23 (and 147), 24, 43, 108, 151.



and other sulphides, such as the sulphides obtained in Experiments 50, 51, 53.



and numerous other chlorides, as illustrated by Experiments 65, 66, 67, 68, or, when an element or a compound body combines with a compound to form a more or less complex compound body: e.g.,



also illustrated by the reactions involved in Experiments 75, 77, 82, 95 (and 97), 118, 139,



and by those of Experiments 27 (101 and 104), 74, 83, 84, 103, 113, 126, 129 (and 130), 135, 136, 137, 159.

(No equations are given for these reactions, as the student will have no difficulty in expressing the changes symbolically.)

One of the most important groups of bodies, viz., the **metallic oxides**, is formed by the combination of metals with oxygen—a chemical change which is a true process of *combustion*, accompanied by the evolution of much heat. The following are the conditions which are most favourable to such a change:—

1st. *The metal should be in a finely divided state; e.g., in the form of powder, or as thin wire or foil.*

Copper wire, or thin zinc foil, burns in a Bunsen gas flame; i.e., the metals combine with oxygen to form cupric and zinc oxide. Iron obtained by the reduction of ferric oxide, in a current of dry hydrogen gas—so-called pyrophoric iron—is oxidized by air at the ordinary temperature.

2nd. *A metal which forms a fusible oxide burns more readily because a fresh surface of unoxidized metal is constantly exposed to the oxygen.*

3rd. *A volatile metal, i.e., a metal which can be readily converted into vapour, such as sodium, zinc, magnesium, cadmium, combines with oxygen more readily than a metal with difficulty volatilized, such as silver, copper; because the two elements are brought together in the gaseous state, and the contact between their particles is thereby greatly promoted (Experiments 19 and 20).*

4th. *Many metals which at the ordinary temperature are not acted upon by dry air, are rapidly oxidized in a moist atmosphere, containing traces of carbonic anhydride.*

Iron, for example, rusts rapidly in moist air.

Zinc is protected, after a time, by a film of white oxide. Both these metals oxidize far more rapidly when exposed to acid fumes. Tin plate, i.e., iron coated over with a layer of tin, in order to protect it from rusting, is rapidly

\* A change arising from the rearrangement of the elements, or groups of elements, already contained in a body, so as to form isomeric compounds, occurs very rarely among inorganic bodies, and may be neglected altogether.

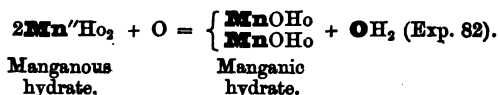
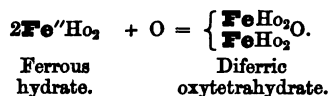
destroyed as soon as the tin coating has become damaged in places, because a voltaic action is set up between the metals tin and iron and the oxygen.

Iron filings when placed in a saucer and moistened with water and left for some time exposed to a moist atmosphere, become covered with red iron rust. The oxidation proceeds at first slowly, at the expense of the oxygen in the air which the water holds in solution, but goes on more rapidly after the metal has become covered with a coating of iron oxide. A faint odour of hydrogen is likewise observed; because the iron forms the electro-positive pole of a voltaic pile—



Water is thus decomposed at the ordinary temperature, and the iron is oxidized simultaneously by the oxygen of the air, dissolved in the water, and by the oxygen of the water itself.

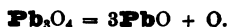
Lower oxides, e.g., ferrous or manganous oxide, are rapidly converted into higher oxides, by the action of the oxygen in atmospheric air, especially in the presence of water, or when they exist already as hydrates—



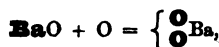
Other lower oxides require to be heated in contact with air; **PbO**, for instance, when heated to 400° C., combines with oxygen to form red lead, **Pb<sub>3</sub>O<sub>4</sub>**—



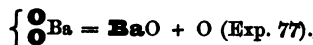
but yields its oxygen again when heated more strongly,—



In like manner also—



and on further heating—

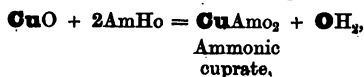


**Combination and resolution** being, in these instances, merely a question of temperature.

5th. *Many metals whose oxides combine with alkali bases, and play the part of an acid, are all the more rapidly acted upon by oxygen when in contact with alkalies, or in the presence of the vapour of ammonia.*

**Experiment 170.**—Fill a test-tube with oxygen and bright copper turnings, and invert it over a small dish containing a strong solution of ammonia. The colourless liquid becomes gradually blue, and is seen to rise slowly in the tube, till the whole test-tube is filled with it.

Copper is but little acted upon by moist atmosphere; not so, however, when placed in a gaseous mixture containing oxygen and ammonia. The chemical change is induced by the tendency of cupric oxide to dissolve in ammonia to a blue liquid, and to form a chemical compound of a quasi-saline nature:—



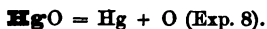
Metals may be divided, according to the facility with which they become oxidized, and displace hydrogen in water, as follows :—

Metals whose oxides are not decomposed by heat alone.				Metals whose oxides are decomposed by heat alone.
I. Metals which combine with oxygen at all temperatures, and which decompose water at the lowest temperature, with evolution of hydrogen.	II. Metals which combine with oxygen only at an increased temperature, and which decompose water at 100° C., or, in the presence of an acid, in the cold, hydrogen being given off. Some (Al, Zn, Cd) decompose potassic hydrate, with evolution of hydrogen.	III. Metals which combine with oxygen at a red heat, and which decompose water (steam) at a red heat: but are not oxidized by water in the presence of strong acids. Their oxides act as acids in the presence of strong alkali bases. Tin decomposes potassic hydrate, on boiling, with evolution of hydrogen.	IV. Metals which combine with oxygen at a red heat and decompose water (steam) to a slight degree, and only at a very high temperature. They do not decompose water in the presence of strong acids or alkalis at the ordinary temperature.	V. Metals which do not combine with oxygen directly, and which do not decompose water under any conditions. They are sometimes called noble metals.
Potassium. Sodium. Barium. Strontium. Calcium.	Magnesium. Aluminium. Manganese. Iron. Chromium. Nickel. Cobalt. Zinc. Cadmium.	Tin. Antimony.	Copper. Lead. Bismuth.	Mercury. Silver. Platinum. Gold.

The power which metals possess of combining with sulphur, chlorine, &c., varies likewise greatly in degree and intensity, according to the nature and state of division of the metal, and according to temperature. Most metals, as we have seen in Chapters VIII and IX, combine directly with chlorine and sulphur, and their respective chlorides and sulphides resist decomposition by heat, with the exception of those of the noble metals, gold and platinum.

*Matter undergoes a chemical change—*

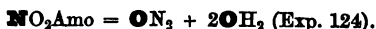
**II. When a compound body resolves itself into its component elements; or into an element and a compound body; or, lastly, into two or more less complex compound bodies: e.g.,**



Other reactions of a like nature will be found in Experiments 33 (34, 35, and 36), 69, 133.



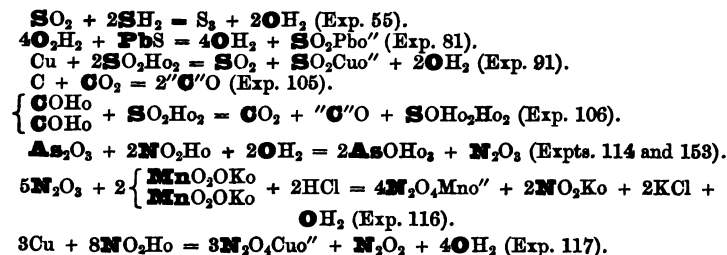
Further illustrations will be found in Experiments 18, 75, 79, 125.



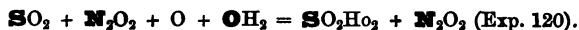
Also illustrated by the analogous reactions of Experiments 148 and 149.

**Resolution** is often accompanied by **combination** in the presence of an

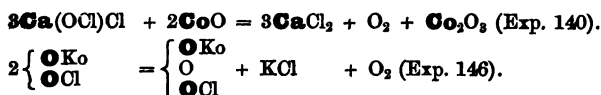
element or a compound body, which exerts an affinity for one of the elements *e.g.*,



Likewise the reactions involved in the manufacture of sulphuric acid :—

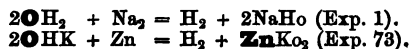


As well as in the following chemical changes :—



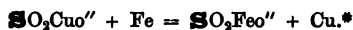
### III. When an element or group of elements in a body is displaced by another element or group of elements.

This change comprises many interesting reactions based upon the displacement of a less electropositive by a more electropositive element: *e.g.*,

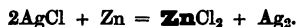


Reactions of an analogous nature are illustrated by Experiments 31, 62, 63, 71, 134.

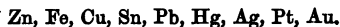
Iron displacing copper in copper salts :—



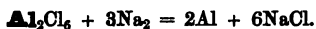
Zinc or copper displacing silver in silver salts :—



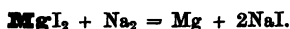
The more electropositive metal displacing, in fact, the less electropositive in the following order :—



In the dry way, the more electropositive metal sodium, when heated with dry aluminic chloride,  $\text{Al}^{12}_2\text{Cl}_6$ , yields aluminium and sodic chloride :—



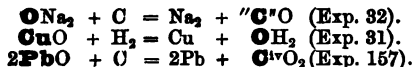
Magnesium iodide, when heated with sodium, yields magnesium :—




---

\* Some illustrations of chemical changes are used in this chapter with which the student has not yet become acquainted. They will be explained in the second volume of the Text-book.

Hydrogen, carbon, or carbonic oxide, set free the metal in metallic oxides, *e.g.*,

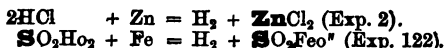


A change of this kind is usually termed a **reduction**. Hydrogen displaces metals from most oxides only at a high temperature. It is without action upon the oxides of potassium, sodium, barium, strontium, calcium, aluminium. The oxides of mercury, silver, platinum, and gold are reduced by hydrogen at a temperature a little above  $100^\circ \text{C}$ .; whilst the other oxides are for the most part only reduced at a red heat.

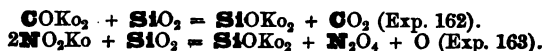
The oxides of iron are reduced to metallic iron by hydrogen with formation of steam; and yet one of the methods for preparing hydrogen consists in passing steam over iron-turnings, placed in a gun-barrel and heated in a furnace. This curious *reciprocal* action depends evidently upon the relative quantities of iron oxide and hydrogen, and of metallic iron and steam, which are acted upon. In the one case the steam formed by the reduction of the ferric oxide in a current of hydrogen is immediately carried along by the excess of hydrogen gas and removed out of contact with the reduced metal; in the second the steam is largely in excess and carries along the liberated hydrogen. Temperature likewise influences these changes.

In carbon we possess a most powerful reducing agent. It reduces not only all oxides which are decomposed by hydrogen, but likewise, at a white heat, oxides which are not reduced by hydrogen, *e.g.*,  $\text{OK}_2$ ,  $\text{ONa}_2$  (Exp. 32).

An element or group of elements can displace another element or group of elements, with formation of salts; as when an acid is made to act upon different metals, *e.g.* :—

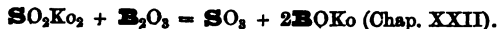


or when silicic anhydride is fused with potassic carbonate or nitre :—

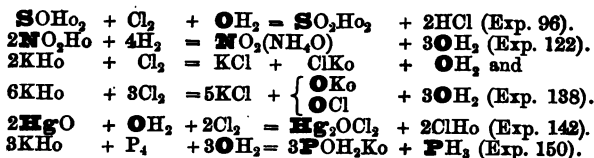


the second reaction being accompanied by **resolution**.

The more volatile acid, as a rule, is driven out or displaced by the less volatile body, *e.g.* :—



**Displacement** is often facilitated by **combination**, as in the case of the following reactions :—



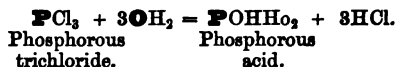
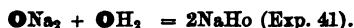
*Matter undergoes lastly a chemical change—*

#### IV. When a mutual exchange of elements or groups of elements in two or more bodies takes place.

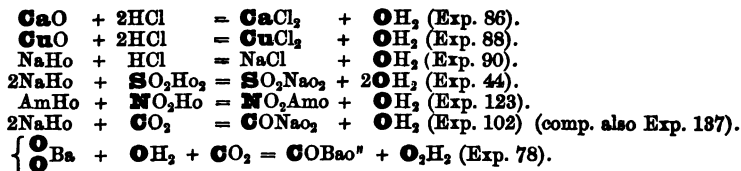
These are often designated changes by **double decomposition**. A great number of chemical bodies originate in an exchange of this kind.

It enables us, for instance, to convert—

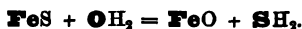
*a. Oxides and chlorides into hydrates, by the action of water or alkaline hydrates, e.g. :—*



*b. Oxides or hydrates into chlorides, sulphates, &c., by the action of hydrochloric or sulphuric, &c., acids, e.g. :—*



*c. Sulphides into oxides, by the action of water (steam), e.g. :—*



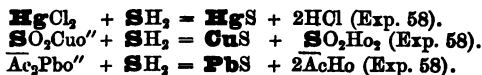
*d. Oxides or hydrates into sulphides, by means of sulphuretted hydrogen, e.g. :—*



*e. Sulphides into chlorides and sulphates, by means of hydrochloric or sulphuric acid, e.g. :—*



*f. Chlorides, &c., into sulphides, by the action of sulphuretted hydrogen, e.g. :—*



On adding an acid to a solution of a salt—

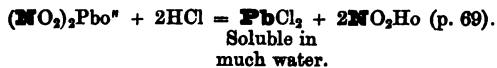
*a.* A mutual exchange takes place, which is frequently imperceptible to the eye, or is indicated only by a change in the colour of the liquid, as when a solution of  $\text{NO}_2\text{Ko}$  is treated with dilute  $\text{SO}_2\text{Ho}_2$ . No signs of decomposition are observed; but on evaporation,  $\text{SO}_2\text{Ko}_2$  crystallises out, it being less soluble than  $\text{NO}_2\text{Ko}$ . Nitric acid, on the other hand, is capable of decomposing potassic sulphate, provided the evaporation be conducted at a sufficiently low temperature ( $0^\circ \text{C.}$ ), at which  $\text{NO}_2\text{Ko}$  is less soluble than  $\text{SO}_2\text{Ko}_2$ .

On adding a solution of hydrochloric acid to a solution of cupric sulphate, the exchange expressed by the equation—

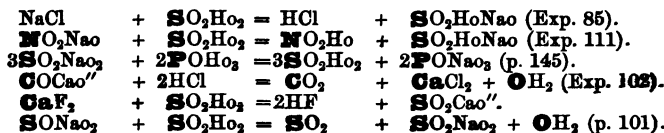


is merely marked by a change of colour, from light blue (the colour of a solution of  $\text{SO}_2\text{CuO}''$ ) to green (the colour of  $\text{CuCl}_2$ ).

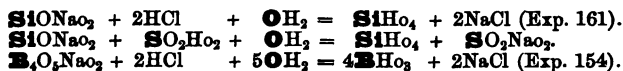
*b.* The acid which is added forms with the base of certain salts a scarcely soluble compound, which is not precipitated from a dilute solution, e.g. :—



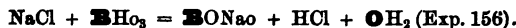
c. A *volatile acid* (or anhydride) is evolved, either at the ordinary temperature or on the application of heat, *e.g.* :—



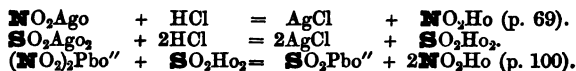
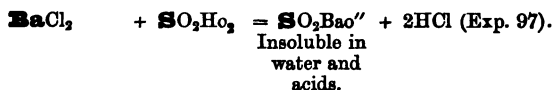
d. The *acid* is liberated from the salt and is nearly *insoluble* in water (no change may possibly be observed in dilute solutions), *e.g.* :—



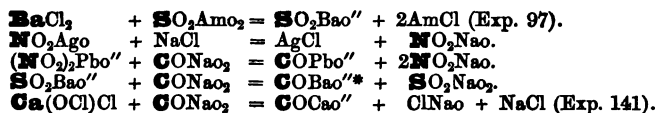
or by a reciprocal change :—



e. A *precipitate* is produced, owing to the insolubility of one of the groups of elements (produced by a mutual exchange between salt and acid), *e.g.* :—



A similar exchange of elements frequently takes place when a solution of one salt is added to a solution of another salt, *e.g.* :—



The mutual exchange of elements between two salts need not necessarily be accompanied by the precipitation of a group of elements, *e.g.* :—



It suffices frequently if the new compound be rendered less soluble, than either of the two salts which were mixed together, *e.g.*,

A solution of KCl and  $\text{NO}_2\text{NaO}$ , when evaporated at a low temperature, yields the two salts unchanged; KCl crystallises out first. But on boiling the solution of the two salts, NaCl crystallises out, and  $\text{NO}_2\text{Ko}$  remains in solution, being more soluble than NaCl (comp. Chap. XXIII). On drawing off the boiling solution from the crystallised NaCl, potassic nitrate crystallises out on cooling.

Then, again, on mixing solutions of NaCl and  $\text{SO}_2\text{Mgo}''$ , it is impossible to say how the acids and bases remain combined. They may exist,

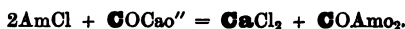
- 1st, as NaCl and  $\text{SO}_2\text{Mgo}''$ ,
- 2nd, as  $\text{MgCl}_2$  and  $\text{SO}_2\text{NaO}_2$ ,
- 3rd, as NaCl,  $\text{MgCl}_2$ ,  $\text{SO}_2\text{NaO}_2$ ,  $\text{SO}_2\text{Mgo}''$ ;

---

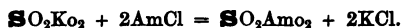
\* By fusion with fusion-mixture, or by long-continued boiling with alkaline carbonates.

but on evaporating the solution above 15° C., NaCl crystallises out first (being the least soluble of the above salts at this temperature), and  $\text{SO}_2\text{Mg}''$  next, mixed with a little NaCl. When evaporated at a lower temperature, *e.g.*, at 0° C.,  $\text{SO}_2\text{NaO}_2$  (being the least soluble at this low temperature) crystallises out first, and leaves  $\text{MgCl}_2$  in solution.

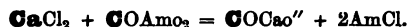
Heat promotes the exchange of elements between two salts of different acids and bases, *e.g.*,



The change is owing to the volatile nature of ammonic carbonate,



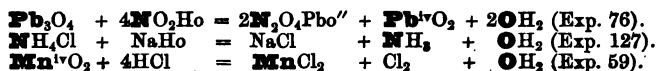
These decompositions are frequently the reverse of the reactions which take place in the cold, between the solutions of two salts, *e.g.*,



owing to the insolubility of the calcic carbonate.

Heat promotes likewise the formation of double silicates and borates, fluorides and chlorides. These compounds are frequently broken up again on being dissolved in water, the original salts being produced.

In a few instances **double decomposition** is accompanied by **resolution**, *e.g.* :—



For purposes of reference, the four different changes just enumerated may be indicated by employing the bracketed letters—

- |      |                        |  |
|------|------------------------|--|
| (C)  | standing for Change I, | <i>i.e.</i> , <b>Combination.</b>              |
| (R)  | „ „                    | II, <i>i.e.</i> , <b>Resolution.</b>           |
| (D)  | „ „                    | III, <i>i.e.</i> , <b>Displacement.</b>        |
| (DD) | „ „                    | IV, <i>i.e.</i> , <b>Double Decomposition.</b> |



## APPENDIX.

### THE METRIC SYSTEM.

#### *Measures of Length.*

Millimètre .....	0·001 of a mètre.....	0·0394 inch.
Centimètre.....	0·01 „ .....	0·3937 „
Decimètre .....	0·1 „ .....	3·9370 inches.
Mètre.....	1 mètre .....	39·37 „
Decamètre .....	10 mètres .....	393·7 „
Hectomètre .....	100 „ .....	328·09 feet.
Kilomètre .....	1000 „ .....	3280·9 „
Myriamètre .....	10000 „ .....	6·2138 miles.

#### *Measures of Surface.*

Centiare.....	1 square mètre .....	1550 square inches.
Are.....	100 square mètres.....	119·6 square yards.
Hectare .....	10000 „ „ .....	2·471 acres.

#### *Measures of Capacity.*

Millilitre, or cubic } centimètre .....	0·001 of a litre.....	0·061 cubic inch.
Centilitre .....	0·01 „ .....	0·61 „ „
Decilitre.....	0·1 „ .....	0·176 imperial pint.
Litre .....	1 cubic decimètre ..	1·76 „ „
Decalitre.....	10 „ „ ..	2·2 „ „
Hectolitre .....	100 „ „ ..	22·009 „ „
Kilolitre (stère).....	1000 „ „ ..	220·096 „ „

#### *Weights.*

Milligramme ....	0·001 wt. 1 cu. m.m. water	0·01543 grains avoird.
Centigramme....	0·01 „ 10 „ „	0·15432 „ „
Decigramme ....	0·1 „ 0·1 „ c.m. „	1·54323 „ „
Gramme.....	1 „ 1 c.c. „	15·43235 „ „
Decagramme ....	10 „ 10 „ „	0·2204 lb. avoird.
Hectogramme ..	100 „ 1 decilitre „	22046 „ „
Kilogramme ....	1000 „ 1 litre „	2·20462 „ „
Myriagramme ..	10000 „ 10 litres „	22·04621 „ „
Quintal .....	100000 „ 1 hectolitre „	220·46 „ „
Tonneau.....	1000000 „ 1 cub.mètre „	2204·6 „ „

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